

FINAL REPORT

Corrosion Finishing/Coating Systems For DoD Metallic Substrates Based on Non-Chromate Inhibitors and UV Curable, Zero VOC Materials

SERDP Project WP-1519

AUGUST 2010

Prof. Matt O'Keefe
Missouri S&T

This document has been approved for public release.



Report Documentation Page				Form Approved OMB No. 0704-0188	
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE AUG 2010		2. REPORT TYPE		3. DATES COVERED 00-00-2010 to 00-00-2010	
4. TITLE AND SUBTITLE Corrosion Finishing/Coating Systems For DoD Metallic Substrates Based on Non-Chromate Inhibitors and UV Curable, Zero VOC Materials				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Missouri S&T,Rolla,MO,65409				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT Corrosion resistant coatings containing non-chromate inhibitors and no volatile organic compounds were developed and evaluated for DoD applications. The technical effort involved cerium based conversion coatings (CeCCs) and ultraviolet (UV) light curable coatings containing corrosion inhibitors. This approach would replace the current three layer, environmentally unfriendly coating system with a benign, two layer multifunctional UV (MUV) coating system. Replacement of corrosion coatings on high strength aluminum alloys used for military aerospace applications was the main focus for the technology developed. Work on the impact of processing parameters on CeCC corrosion performance, including the use of gelatin in the deposition solution and post deposition treatment in phosphate solution, resulted in significant improvement in CeCC protection of high strength aluminum from corrosion. The identification of sub-surface crevices in the Al substrates that form during CeCC deposition helped explain results previously not understood. Application of MUV coatings with Hybricor 204 corrosion inhibitor repeatedly demonstrated the ability to protect scribed, chromate conversion coated Al substrates during ASTM B117 salt spray testing. Drawbar applied MUV coatings on CeCC passed salt spray testing while spray applied MUV on CeCC formed blisters during ASTM B117 testing. MUV coating properties such as flexibility and fluid resistance were improved throughout the project and demonstrated the potential to meet aerospace requirements. Results indicate that the technology holds promise for replacing existing environmentally hazardous corrosion coatings for military applications.					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Same as Report (SAR)	18. NUMBER OF PAGES 78	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

Table of Contents

	Page
List of Acronyms	iii
List of Figures and Tables	iv
Acknowledgments	x
1. Abstract	1
2. Objective	2
3. Background	2
3.1 Non-Chromate Cerium Based Conversion Coatings	3
3.2 Zero VOC Coatings	4
3.3 UV Curable Coatings	4
4. Materials and Methods	6
4.1 Pre-Treatment Conversion Coatings	6
4.2 Substrate Materials	6
4.3 MUV Curable Coatings	6
4.4 Integrated Coating Systems	7
4.5 Characterization	9
5. Results and Discussion	10
5.1 Health and Safety Assessment	10
5.2 Cerium-based Conversion Coatings	10
5.3 Multifunctional UV (MUV) Curable Coatings	36
6. Conclusions and Implications for Future Research/Implementation	64
7. Literature Cited	66
8. Appendices	67
8.1 List of Scientific/Technical Publications	67
A. Articles in Peer-Reviewed Journals	67
B. Technical Reports	67
C. Conference or Symposium Scientifically Recognized	68
D. Conference or Symposium Abstracts	68

List of Acronyms

AES – Auger Electron Spectroscopy
ASTM – American Society for Testing and Materials
CeCC – Cerium Conversion Coatings
CrCC – Chromate Conversion Coatings
DoD – Department of Defense
EDS – Energy Dispersive Spectroscopy
EIS – Electrochemical Impedance Spectroscopy
EPA – Environmental Protection Agency
FIB – Focused Ion Beam
HALS – Hindered Amine Light Stabilizers
HAPs – Hazardous Air Pollutants
HMIS – Hazardous Materials Identification System
IBOA – Isobornyl Acrylate
LCC – Light Curable Coatings
MUV – Multifunctional UV
NCLT – Non-Chromated, Low Temperature
OSHA – Occupational Safety and Health Administration
PEA – Phenoxyethyl Acrylate
PEL – Permissible Exposure Limit
SEM – Scanning Electron Microscopy
SERDP – Strategic Environmental Research and Development Program
TCP – Trivalent Chromium Passivation
TEM – Transmission Electron Microscopy
TRI – Toxic Release Inventory
UV – Ultraviolet
UVAs – Ultraviolet Absorbers
VOCs – Volatile Organic Compounds
XPS – X-ray photoelectron spectroscopy
XRD – X-ray Diffraction

List of Figures and Tables

<u>Figures</u>	<u>Page</u>
Figure 1. Left: Existing three layer, hexavalent chromium based corrosion coating system. Right: Two layer non-chromate, multifunctional UV (MUV) curable corrosion coating system under development.	2
Figure 2. Auger Electron Spectroscopy depth profiles of spray coated samples cleaned at (a) 45°C, (b) 55°C, and (c) 65°C showing that the cerium oxide thickness increased with cleaning temperature.	12
Figure 3. Optical images of alkaline cleaned Al 2024-T3 substrates after 6, 12, and 25 spray cycles.	13
Figure 4. Optical images of an acid cleaned Al 2024-T3 substrates after 1 spray cycle.	13
Figure 5. Auger depth profiles of Al 2024-T3 panels after (a) alkaline and (b) acid cleaning.	14
Figure 6. Nyquist plots for aluminum 7075-T6 panels prepared using different methods.	15
Figure 7. Nyquist plots for aluminum 7075-T6 panels with CeCCs deposited on panels prepared using each method.	16
Figure 8. Optical images of prepared, uncoated aluminum 7075-T6 panels after exposure to salt fog for 18 hours A) chemical immersion, B) chemical wipe, C) ultrasonic processing, and D) abrasive blasting.	17
Figure 9. Optical images of coated aluminum 7075-T6 panels after exposure to salt fog for 18 hours A) chemical immersion, B) chemical wipe, C) ultrasonic processing, and D) abrasive blasting.	18
Figure 10. SEM micrographs of CeCC deposited using pH 2.5 and pH 1.0 spray solutions.	19
Figure 11. Plot of wt.% Ce detected by EDS vs. wt.% of Ce in the spray solution.	20
Figure 12. Plot of wt.% Ce detected by EDS vs. ml of H ₂ O ₂ in the spray solution.	20
Figure 13. Nyquist plots of CeCC Al 2024-T3 panels in prohesion solution after 3 hours of testing for panels deposited using 1, 2, 3, and 4 wt.% Ce in the deposition solution.	21

Figure 14. Nyquist plots of CeCC Al 2024-T3 panels in prohesion solution after 3 hours of testing for panels deposited using 0, 5, 10, and 20 ml of H_2O_2 in the deposition solution.	22
Figure 15. Images of CeCC Al 2024-T3 samples deposited using 0, 5, 10, and 20 ml of H_2O_2 in the spray solution following 5 hours of EIS testing in prohesion solution.	22
Figure 16. a) Scanning electron micrograph of a CeCC deposited on an Al 2024-T3 panel with no gelatin in the spray solution; b) optical image of panel after 2 days of salt spray testing.	24
Figure 17. Auger depth profile of a 5 spray cycle CeCC deposited on an Al 2024-T3 panel with no gelatin in the spray solution.	24
Figure 18. a) Scanning electron micrograph of a CeCC deposited on an Al 2024-T3 panel with 3200 ppm gelatin in the spray solution; b) optical image of panel after 7 days of salt spray testing.	25
Figure 19. Auger depth profile of a 5 spray cycle CeCC deposited on an Al 2024-T3 panel with 3200 ppm gelatin in the spray solution.	25
Figure 20. Electrochemical impedance of CeCC deposited on an Al 2024-T3 panel with 3200 ppm and no gelatin (0 ppm) in the spray solution.	26
Figure 21. a) Scanning electron micrograph of an as deposited (unsealed) CeCC on an Al 2024-T3 panel; b) optical image of panel after 14 days of salt spray testing.	27
Figure 22. a) Scanning electron micrograph of a CeCC post treated in a $NH_4H_2PO_4$ solution at $85^\circ C$ for 5 minutes on an Al 2024-T3 panel; b) optical image of panel after 14 days of salt spray testing.	27
Figure 23. Electrochemical impedance of CeCCs on Al 2024-T3 panels post treated in different phosphate solutions.	28
Figure 24. X-ray diffraction patterns of CeCCs post treated in different phosphate solutions, and one not post treated (unsealed), on Al 2024-T3 panels.	28
Figure 25. Coating thickness as a function of the number of brush or spray deposition cycles.	30
Figure 26. XRD spectra for coatings deposited using three, five, and seven brush cycles, and three and five spray cycles.	30

Figure 27. Schematic drawing of reactions that increase the pH near the surface of Al substrates that causes cerium precipitation from solution.	31
Figure 28. Schematic drawing of reactions that occur during CeCC precipitation from solution.	32
Figure 29. Electron micrograph image of a CeCC on an Al 2024-T3 panel after FIB sectioning.	33
Figure 30. Cross sectional micrograph image of an Al 2024-T3 panel after cleaning (no sub- surface crevices).	33
Figure 31. Cross sectional micrograph image of an Al 2024-T3 panel after CeCC deposition (contains sub-surface crevices).	34
Figure 32. Cross sectional micrograph image of an Al 2024-T3 panel after spraying a $\text{H}_2\text{O}_2 + \text{NaCl}$ solution on the surface.	35
Figure 33. Cross-sectional TEM images of cerium based conversion coatings: a) as-deposited, b) after 14 days of salt spray testing.	36
Figure 34. Auger electron spectroscopy depth profiles of cerium based conversion coatings: a) as-deposited and b) after 14 days of salt spray testing	36
Figure 35. Optical images of Stage 1 Al 2024-T3 coated panels after 3000 hours of neutral salt spray testing.	38
Figure 36. Optical images of Stage 1 Al 2024-T3 coated panels after 3000 hours of neutral salt spray testing and removal of the corrosion coatings.	39
Figure 37. Auger maps for Cr, Al, and Zn near the scribe for two different Hybricor 204 MUV coated panels; one not exposed to salt spray and the other after passing 3000 hours salt spray.	41
Figure 38. Auger maps for Ce, Al, and Zn near the scribe for two different Hybricor 204 MUV coated panels; one not exposed to salt spray and the other after passing 3000 hours salt spray.	42
Figure 39. Optical images of Round 2 Al 2024-T3 coated panels after 2000 hours of neutral salt spray testing.	43
Figure 40. Optical image of a Round 2 Hybricor 204 MUV coated Al 2024-T3 panel with a TCP conversion coating after 2000 hours salt spray	44
Figure 41. Optical image of a Round 2 Hybricor 204 MUV coated Al 2024-T3 panel that did not have a conversion coating (bare) after 2000 hours salt spray.	44

Figure 42. Images of integrated coatings on CrCC Al clad Al 2024-T3 after 1000 hours of filiform corrosion testing	45
Figure 43. Optical images of MUV coated Al 2024-T3 panels with different charge levels of Hybricor 204 corrosion inhibitor after 3000 hours of salt spray testing.	46
Figure 44. Optical images of MUV coated Al 2024-T3 panels on CeCC and CrCC pretreatments.	48
Figure 45. Optical images of wet scribe test results.	49
Figure 46. Optical images of Al 2024-T3 control panels after 3000 hours of salt spray corrosion testing.	50
Figure 47. Optical images of MUV coated Al 2024-T3 panels with CrCC and CeCC pretreatments after 3000 hours of salt spray corrosion testing.	51
Figure 48. Optical images of MUV coated Al 2024-T3 panels with TCP pretreatments after 3000 hours of salt spray corrosion testing.	52
Figure 49. Optical images of Al 7075-T6 control panels after 3000 hours of salt spray corrosion testing.	53
Figure 50. Optical images of MUV coated Al 7075-T6 panels with CrCC and CeCC pretreatments after 3000 hours of salt spray corrosion testing.	54
Figure 51. Al 2024-T3 chromate control panels after 3000 hours ASTM B117 testing.	59
Figure 52. Al 2024-T3 panels with MUV on CrCC after 3000 hours ASTM B117 testing.	59
Figure 53. Optical images of Al 2024-T3 panels after 2000 hours of ASTM B117 salt spray testing: a) chromate standard and b) MUV on CrCC.	60
Figure 54. Optical images of Al 2024-T3 panels after 2000 hours of ASTM B117 salt spray testing: a) non-chromate standard, b) MUV on TCP, and c) MUV on CeCC.	61
Figure 55. Optical images of Al 2024-T0 panels after low temperature flexibility tests.	62
Figure 56. Optical images of Al 2024-T0 panels after room temperature flexibility tests: a) chromate controls and b) MUV on CrCC.	62

<u>Tables</u>		<u>Page</u>
Table I	Health and Safety Assessment of Coating Materials	10
Table II	Summary of CeCC Phosphate Sealing Study	29
Table III	Summary of MUV Testing	37
Table IV	Coating Systems Evaluated (Round 3)	47
Table V	Test Matrix for MUV/CeCC Panels Done at LCC Oct 2008	55
Table VI	Pencil Hardness, Adhesion, Gloss, MEK Rub and Skydrol Results for MUV/CeCC Panels Done at LCC Oct 2008	56
Table VII	Salt Spray Ratings for MUV/CeCC Panels Done at LCC Oct 2008	58
Table VIII	Summary of MUV Evaluation Results	63

Acknowledgments

Thanks are due to the many people that contributed to this effort. The project was co-managed by Bill Fahrenholtz (Missouri S&T), Ben Curatolo (Light Curable Coatings), and John DeAntoni (Boeing). Jim Stoffer's contributions and dedication to the project while in retirement is both admirable and appreciated. The work done by graduate students Will Pinc, Simon Joshi, Daimon Heller, William Gammill, Phillip Jones, and Andrew Thomas along with post-doctoral fellows Dr. Ajay Padwal, Dr. Shujiang Geng, Dr. Becky Treu, Dr. Surender Maddela, and Dr. Beth Kulp at Missouri S&T has been of the highest quality. The support of the staff of the Graduate Center for Materials Research Center at Missouri S&T is gratefully acknowledged. Thanks are extended to Donna Ballard at AFRL/ML in the first few years of the project and Gary Wright of AFRL/ML in the final year for their support and encouragement. The contributions of Dr. Paul Yu and Prof. Tom O'Keefe from the start of the project until the spring of 2008 are acknowledged in memoriam.

The financial support of the Strategic Environmental Research and Development Program and guidance of program managers Chuck Pellerin and Bruce Sartwell are gratefully acknowledged.

1. Abstract

Corrosion resistant coatings containing non-chromate inhibitors and no volatile organic compounds were developed and evaluated for DoD applications. The technical effort involved cerium based conversion coatings (CeCCs) and ultraviolet (UV) light curable coatings containing corrosion inhibitors. This approach would replace the current three layer, environmentally unfriendly coating system with a benign, two layer multifunctional UV (MUV) coating system. Replacement of corrosion coatings on high strength aluminum alloys used for military aerospace applications was the main focus for the technology developed. Work on the impact of processing parameters on CeCC corrosion performance, including the use of gelatin in the deposition solution and post deposition treatment in phosphate solution, resulted in significant improvement in CeCC protection of high strength aluminum from corrosion. The identification of sub-surface crevices in the Al substrates that form during CeCC deposition helped explain results previously not understood. Application of MUV coatings with Hybricor 204 corrosion inhibitor repeatedly demonstrated the ability to protect scribed, chromate conversion coated Al substrates during ASTM B117 salt spray testing. Drawbar applied MUV coatings on CeCC passed salt spray testing while spray applied MUV on CeCC formed blisters during ASTM B117 testing. MUV coating properties such as flexibility and fluid resistance were improved throughout the project and demonstrated the potential to meet aerospace requirements. Results indicate that the technology holds promise for replacing existing environmentally hazardous corrosion coatings for military applications.

2. Objective

The primary objective of this project was to research, develop, characterize, evaluate, integrate, and demonstrate an environmentally friendly, chromate-free, zero TRI/VOC/HAPs coating system using rare-earth oxide based pretreatments and corrosion inhibiting, multifunctional UV (MUV) curable self-priming coatings for metallic substrates that meet or exceed current military requirements. The integrated two layer non-chromate coating system replaces the existing three layer system (Figure 1), and utilization of a UV curing system will greatly reduce the time required to paint DoD equipment. Aluminum alloy substrates commonly used in military aerospace applications were the main focus of the work. The integration, compatibility, and effectiveness of the novel low and high gloss ultraviolet light curable, corrosion preventing, MUVs with rare-earth based conversion coatings has the potential to meet or exceed all of the objectives contained in the SERDP statement of need PPSON-06-04.

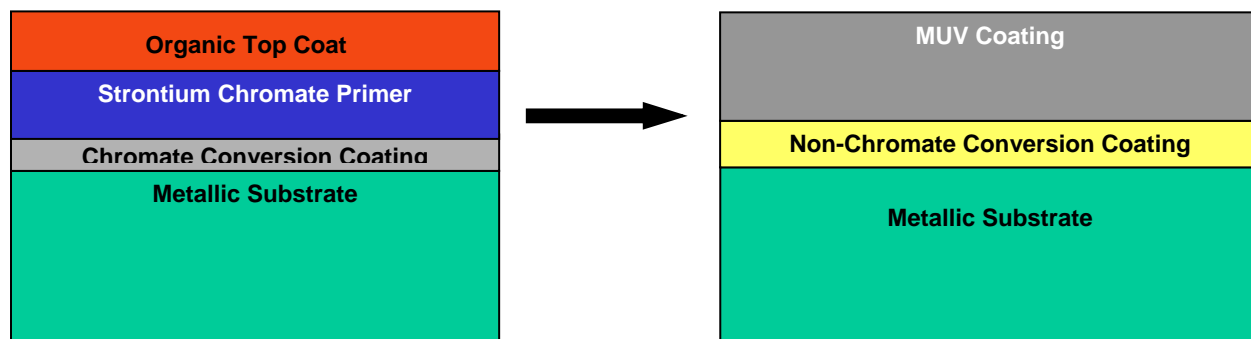


Figure 1. Left: Existing three layer, hexavalent chromium based corrosion coating system. Right: Two layer non-chromate, multifunctional UV (MUV) curable corrosion coating system under development.

3. Background

Military corrosion protection coating systems typically consist of a metal pretreatment conversion coating followed by an epoxy primer and a polyurethane topcoat. Although very effective at preventing corrosion of the underlying metallic substrate, these coatings contain volatile organic compounds (VOCs), hazardous air pollutants (HAPs) and chemicals listed on the toxic release inventory (TRI). The chromate corrosion inhibitors used in the conversion coating in direct contact with the metallic substrate, as well as in the epoxy primer, present a serious health risk to workers that paint and de-paint military assets. In addition, the epoxy primer is formulated at 340 grams per liter VOC while polyurethane topcoats are typically formulated at 420 grams per liter VOC and are crosslinked with hazardous isocyanates that are on the TRI.

The annual cost of corrosion to the U.S was estimated at \$276 billion dollars. According to the “Cost of Corrosion” study published by CC Technologies and NACE International, corrosion and metal wastage arising from oxidation as caused by exposure to the elements and reactivity between dissimilar materials costs the U.S. military about \$20 billion annually [1]. Aluminum alloys important in both military and civilian aircraft are prone to such corrosion. The result is an annual maintenance cost for Navy aircraft of about \$800 million per year. According to USAF

sources, aircraft painting/stripping/repainting processes and handling associated hazardous waste is one of the highest cost maintenance activities. Chromates are an essential part of the present coating systems used on many DoD substrates.

The EPA regulates chromium and its compounds under the Clean Air Act, Clean Water Act, Comprehensive Environmental Response, Compensation and Liability Act, Resource Conservation and Recovery Act, Superfund Amendments and Reauthorization Act, and Toxic Substances Control Act. Federal, state, and local agencies have issued regulations that limit or prohibit the use of chromate-containing materials. OSHA regulates the amount of hexavalent chromium to which workers can be exposed and has reduced the Permissible Exposure Limit (PEL) for hexavalent chromium and for all Cr(VI) compounds in construction, shipyards, and general industry from the previous $52 \mu\text{g}/\text{m}^3$ to $5 \mu\text{g}/\text{m}^3$ as an 8 hour time-weighted average [2]. This also includes provisions for employee protection such as preferred methods for controlling exposure, respiratory protection, protective work clothing and equipment, hygiene areas and practices, medical surveillance, hazard communication, and record keeping. These regulations will severely impact the use of hexavalent chromium throughout the DoD and the defense industry. Use of hexavalent chromium compounds is also tightly controlled by EPA regulations issued under the Toxic Substances Control Act, Safe Drinking Water Act, Clean Water Act, Clean Air Act, Resource Conservation Recovery Act, Comprehensive Environmental Response, Compensation and Liability Act; and by OSHA under the Occupational Safety and Health Act. Chromium has been found in 1,036 of 1,591 National Priority List (Superfund) sites identified by the EPA. Development of a chrome free alternative corrosion protection coating system would not be subject to these restrictions while maintaining the corrosion protection needed for DoD platforms.

There has been extensive research on the development of alternative treatments of metallic surfaces for corrosion protection. Among the major classes of chromate alternatives are cerium, cobalt, molybdenum, and manganese-based coatings, titanium and zirconium fluorocomplexes, hydrotalcites, boehmites and silanes, and inherently conducting polymers. Recent work includes some of the current efforts investigating the use of magnesium rich primers and conducting polymers to protect aluminum alloys, controlled release of inhibitors from polyaniline conductive polymers, and the use of cerium modified bentonite clay for corrosion inhibition and sensing.

3.1 Non-Chromate, Cerium Based Conversion Coatings

The non-chromate coatings group at Missouri S&T has identified cerium compounds as potentially viable corrosion inhibitors and replacements for chromate conversion coatings on aluminum alloys. Success in developing the technology has led to several patent applications being filed and issued [3,4]. Work at Missouri S&T on conversion coatings over the past few years has involved the deposition of cerium oxide-based conversion coatings from aqueous solutions. Feasibility studies on other rare-earth compounds as well as electrochemically active elements have been conducted.

Initial attempts to deposit cerium-based conversion coatings on aluminum alloys consisted of immersion in a cerium chloride solution for a period of several days, which resulted in the deposition of a thin, cerium (III) oxide layer [5]. Some of the methods used to reduce coating deposition time have included galvanostatically polarizing the aluminum surface in an aqueous CeCl_3 bath or boiling the panel in an aqueous cerium salt solution in combination with an anodic treatment in Na_2MnO_4 . The addition of hydrogen peroxide to a cerium chloride bath can reduce the coating time to approximately ten minutes [6]. This method can be further enhanced by the use of a deoxidizer to activate the surface before immersion into the coating bath [7].

Cerium-based conversion coatings have been deposited using electrolytic (current-driven) and spontaneous (immersion) deposition methods. Processes that deposit cerium-based conversion coatings that meet the DoD standard by providing corrosion protection for 336 hours (2 weeks) in ASTM B117 salt spray testing have been developed for both aluminum alloy 7075-T6 and 2024-T3. Mechanistic studies revealed that coating deposition occurred due to an electrochemically-driven increase in the pH near the alloy panel surface that led to the precipitation of insoluble hydrated Ce^{4+} compounds that attached to the panel surface [8]. Work done on this project focused on developing and optimizing a spray process for deposition of cerium-based conversion coatings on aluminum alloy 2024-T3. Based on work done at Missouri S&T, surface preparation, deposition solution composition, and post treatment steps significantly impact the corrosion resistance of cerium oxide conversion coatings.

3.2 Zero VOC Coatings

Zero VOC corrosion coatings can be formulated by substituting VOC exempt solvents that are not photo-chemically reactive. Non-HAP VOC exempt solvents, such as acetone, can be used in coatings formulations. In some cases use of these solvents increases the flammability of the coating and can have a negative impact on appearance and application parameters. More desirable, zero VOC corrosion coatings formulated with water have been introduced to the marketplace, but it is not known if these coatings will meet all of the stringent performance requirements of military specifications, necessitating a different approach.

3.3 UV Curable Coatings

Ultraviolet (UV) light curable coatings are a class of coatings that can be formulated to be solvent free, and therefore zero VOC. UV curing is a photochemical process by which a liquid coating changes to a cross-linked solid polymer through exposure to UV radiation without the need for isocyanate cross-linking agents. Benefits of UV technology include zero VOC, HAPS-free coatings that fully cure in seconds, resulting in faster throughput and labor savings, consistent with the needs outlined in the statement of needs for this project. UV technology is recognized as a Best Available Control Technology and a Lowest Achievable Emission Rate technology by the EPA. An ultraviolet light curable coating qualifies as a “Superclean” technology defined by the Southern California South Coast Air Quality Management District. This allows for immediate installation of UV processes without the need for a permit.

Ultraviolet curing is one of the radiation curing techniques that are used in coatings, inks, adhesives and sealants. UV curable coatings can be formulated to be 100% solids, and can be instantaneously polymerized and cross-linked to give films that are decorative and functional [9].

The original driving forces behind the commercialization of UV-curing technology were energy saving and freedom from solvents [10]. Improved economics, and efficiency result from instantaneous curing characteristic in the case of UV polymerization. Since all of the formulation reacts or remains effectively within the final film, UV curable coatings are near zero VOC. As the pressure to reduce VOC continues to mount, UV cured coatings are becoming more attractive. There are two classes of UV-curable coatings, free radical (mostly acrylate) and cationic (epoxy) depending upon the nature of photoinitiators and resin chemistry.

Improvement in the coating/substrate interaction is one of the most critical areas of performance in the practical application of UV curing. Due to adsorption, the substrate/coating interface receives the lowest dose of UV radiation and the interaction between the coating and the substrate can inhibit the cure [11]. Pigment selection also plays an important role in the overall curing characteristics of pigmented systems. In general, the larger the pigment particle size, the smaller the surface area and, therefore, the better the curing. UV cured coatings that are used for exterior application usually require the use of light stabilizers to prevent degradation of the resin system due to damaging UV radiation. The two light stabilizers typically used are ultraviolet absorbers (UVAs) and hindered amine light stabilizers (HALS). HALS have, in most cases, little or no impact on the cure properties of the photopolymers. UVAs, however, can compete with photoinitiators for the available light and therefore have an impact on the cure speed of most formulations [12]. Incorporation of inorganic corrosion inhibiting compounds into a UV curable matrix results in a multifunctional UV (MUV) coating that provides the weathering protection of a top coat and the corrosion protection of a primer into a single layer.

4. Materials and Methods

The overlap of the technical approach necessitated that all members contributed to each task and significant interaction occurred within each task. Responsibility for the project tasks was distributed by expertise and capabilities in each area, cognizant that each team member contributed to every task. Missouri S&T was the lead organization for non-chromate conversion coatings, LCC headed up the formulation and application of MUV curable coatings, and Boeing was responsible for integration, evaluation and implementation.

4.1 Substrate Materials

Aluminum alloys 2024-T3 and 7075-T6 were used throughout the study. Panels were sheared from large sheets into either 1" x 3" or 3" by 6" size for studies. The bulk chemical composition of Al 2024-T3 is 90.7-94.7 wt% Al, 3.8-4.9 wt% Cu, 1.2-1.8wt% Mg, 0.3-0.9 wt% Mn, maximum of 0.5 wt% Fe, maximum of 0.1wt% Cr, maximum of 0.5wt% Si, maximum of 0.15 wt% Ti, maximum of 0.25 wt% Zn, balance other trace elements. The bulk chemical composition of Al 7075-T6 is 87.1-91.4 wt% Al, 5.1-6.1wt% Zn, 1.2-2.0wt% Cu, 21.-2.9wt% Mg, maximum of 0.3wt% Mn, maximum of 0.5 wt% Fe, 0.18-28wt% Cr, maximum of 0.4wt% Si, maximum of 0.20wt% Ti, balance other trace elements.

4.2 Pre-Treatment Conversion Coatings

Spray deposition of cerium oxide based conversion coatings onto Al 2024-T3 and Al 7075-T6 panel substrates was the focus of the pre-treatment technical efforts. Cleaning of the substrates prior to coating was done by an isopropyl alcohol rinse; an acid, alkaline, or a combination of acid and alkaline solutions; and water rinses. The substrates were kept wet throughout the process. Unless otherwise noted, the deposition solution was 250 ml in volume with a nominal composition of 4 wt.% $\text{CeCl}_3 \cdot x\text{H}_2\text{O}$, 20 ml of 30 vol.% H_2O_2 , 0.8 g of organic gelatin with the balance water. Spray deposition was accomplished using a commercially available detail air gun. The panels were placed upright at an angle of $\sim 60^\circ$ to the horizontal and sprayed evenly for a few seconds, followed by a 35 second delay; this was considered one spray cycle. Repetition of spray cycles was used to build up coating thickness and improve coating uniformity. The hydrated cerium oxide that was deposited by this method was then post treated, or "sealed", in an 85°C phosphoric acid based solution at pH 4.5 to convert the coating, either partially or completely, into hydrated cerium phosphate. All panels were sealed in a phosphate solution unless otherwise noted. Chromate conversion coated panels used for controls during evaluation were produced at Boeing or obtained from commercial vendors.

4.3 MUV Curable Coatings

Several formulations of MUV curable coatings were developed and evaluated throughout the project. Corrosion inhibitors evaluated included Hybricor 204, HT-13, and HT-20 from Wayne Pigments and praseodymium oxide based materials from Deft. The initial studies used 36% inhibitor loading; subsequent ladder studies investigated loadings of 0%, 7%, 15%, 22%, 29% and 36%. Isobornyl acrylate (IBOA) and phenoxyethyl acrylate (PEA) were the two monomers evaluated. Dispersants, fillers, photoinitiators, stabilizers, and other additives were also

evaluated. Five sets (rounds) of MUV coatings were evaluated. The first two rounds were deposited by drawbar with a 36% inhibitor loading. The final three rounds used Hybricor 204 inhibitor at a loading of 29% and were deposited using a spray gun. The MUV formulation was heated to ~105°F prior to spray application in order to produce consistent flow characteristics. Panels were mounted horizontally and the MUV was sprayed using an overlapping pattern until a final film thickness of ~0.002" (2 mils) was achieved. Curing was done sequentially using 10" long, 600W/in V and H ultraviolet lamps from Fusion, Inc. The panels were passed under the bulbs at a conveyor speed of 1"/sec and at a distance of 2.5" from the lamps. This setup resulted in an initial exposure of the panels to a V bulb for about 0.5 second and then to an H bulb for an additional 0.5 second, which fully cured the coatings.

4.4 Integrated Coating Systems

Evaluation of the integrated corrosion coating systems under development against standard test procedures was done throughout the year. Cerium conversion coated panels were made at Missouri S&T and sent to LCC for MUV application in most cases, with one set of panels made at LCC by S&T students in October of 2008. Commercial chromate and non-chromate comparison systems were used as control samples during testing. Evaluation of the coatings were done at Boeing-St. Louis and included neutral salt spray testing, wet adhesion tests, Skydrol fluid resistance, low and room temperature flexibility, filiform corrosion testing, and Xe arc weathering. Boeing's testing procedures are listed below. The ratings criteria for evaluating scribed panels was developed at Boeing to provide a relative performance evaluation; panels with 1,A ratings are considered the best.

Boeing Test Procedures

Surface Treatment:

Coordinate test panel chromate surface treatments with the chemical process area. Cerium conversion coating will be performed by Missouri S&T.

Primer and Topcoat Application:

Apply primer and topcoat per the manufacturer's instructions. Apply primer to dry film thickness between 0.7 and 1.3 mils. Apply topcoat to a dry film thickness between 1.7 and 2.3 mils. Let topcoat air dry two weeks prior to test. Measure and record all coating thicknesses. UV coating will be applied by Light Curable Coatings.

3000 hour 5% salt spray:

Panels shall be scribed with an "X" across the test face using a NewHermes engraving machine. The scribe lines should penetrate to the substrate. Wrap the edges and back of the test panels with tape. Expose the test panels to 5% neutral salt fog for 3000 hours per ASTM B 117.

Check the panels for corrosion at 1000, 2000 and 3000 hours.

For each evaluation period, provide the following:

Rank primers from best to worst.

Rank the panels alpha/numerically using the ranking method established by the laboratory.

Ratings Criteria for Panels after ASTM B117 Testing

Code	Description
1	Scribe line beginning to darken or shiny scribe.
2	Scribe lines > 50% darkened.
3	Scribe line dark.
4	Several localized sites of white salt in scribe lines.
5	Many localized sites of white salt in scribe lines.
6	White salt filling scribe lines.
7	Dark corrosion sites in scribe lines.
8	Few blisters under primer along scribe line. (<12)
9	Many blisters under primer along scribe line.
10	Slight lift along scribe lines.
11	Coating curling up along scribe.
12	Pin point sites/pits of corrosion on organic coating surface (1/16" to 1/8" dia.).
13	One or more blisters on surface away from scribe.
14	Many blisters under primer away from scribe.
15	Starting to blister over surface.

Code	Scribe line ratings - corrosion creepage beyond scribe
A.	No creepage
B.	0 to 1/64
C.	1/64 to 1/32
D.	1/32 to 1/16
E.	1/16 to 1/8
F.	1/8 to 3/16
G.	3/16 to 1/4
H.	1/4 to 3/8

Provide a checklist of all the types of corrosion / defects at each interval:

After the 3000-hour exposure period get photographs taken of the test panels. Strip one of the test panels with Turco 5469 or equivalent paint stripper and get a photograph of the stripped panels.

Scribed Wet Tape Adhesion Tests:

Perform a scribed wet tape adhesion test on the test panels as follows: Scribe two parallel lines with an X-acto knife along the 6" panel direction, approximately 3/4" apart and 2 inches long. Scribe an "X" between the two parallel lines. Apply 3M #250 tape parallel to the first two parallel scribe lines. Roll a 4 lb., 60 durometer rubber roller across the tape 4 times back and forth. Immediately remove the tape at a 45-degree angle with one abrupt motion while holding the panel steady with the opposite hand. Examine the test panel for removal and uplifting of the coating. Evaluate the adhesion of the panels per Method A of ASTM D 3359 - 97 and provide the rating of 5A, 4A, 3A, 2A, 1A, or 0A. Also provide the percentage of the coating removed.

Low Temperature Flexibility:

Expose panels in a cold box maintained at -60°F+/-5°F for 5 hours. After exposure the panels shall be bent over a ½ inch mandrel which has been conditioned at the same temperature. Examine for cracks with unaided eye.

GE Room Temperature Reverse Impact Flexibility:

Using the GE impact tester the flexibility shall be 20% minimum. Test method shall be ASTM D2794. Do not allow the impacter to bounce on the panel. Report results under 10x magnification and with the unaided eye.

1000 Hour Filiform Corrosion:

The test panels shall be scribed with an “X” across the test face using a New Hermes engraving machine. The scribe lines should penetrate to the substrate. Wrap the edges and back of the test panels with tape. Place the panels vertically in a dessicator containing 12N hydrochloric acid for one hour. Within 5 minutes of removal from the desiccator, place the panels in a humidity cabinet maintained at 104 +/- 4 °F and 80 +/- 5% RH for 1000 hours. After removal from the humidity cabinet, examine the test panels for filiform corrosion, as described in ASTM D2803. The applied coating shall exhibit no filiform corrosion extending beyond ¼ in. from the scribe. A majority of the filaments shall be less than 1/8 in. in length. Rank coatings from best to worst. After the 1000-hour exposure period, photograph the test panels. Strip one of the test panels with Turco 5469 or equivalent paint stripper and photograph the stripped panels.

Xenon Arc Weather Resistance:

The test panels shall be exposed for 1000 hours in a xenon-arc weatherometer that is cycling between 102 minutes of light only, and 18 minutes of light and water spray. Check panels for initial color (E value), 85 and 60-degree gloss and at 500 and 1000 hours for Delta E and gloss.

30-day Room Temperature Skydrol Resistance

Determine the initial pencil hardness of the film per ASTM D3363. Scribe the panels and wet with Skydrol LD-4 once daily for 30 days at ambient temperature. Remeasure the pencil hardness after this period. After immersion there shall be no softening below a hardness of H, any blistering, any wrinkling, or loss of adhesion.

4.5 Characterization

Electrochemical and materials characterization techniques were used throughout the project. Surface analysis was done using Auger electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS), imaging and chemical analysis was done using scanning electron microscopes (SEMs) with energy dispersive spectroscopy (EDS) capability, and cross sections were made in a focused ion beam (FIB) microscope. Electrochemical evaluations included potentiodynamic polarization scans and electrochemical impedance spectroscopy (EIS).

Specific details are provided in the publications listed at the end of the report, with articles by S. Geng, et al, “Screening Study of Spray Solution Parameters for Depositing Cerium Based Conversion Coatings on Al Alloy 2024-T3”, J. Applied Electrochemistry, 40, 551, (2010) and W. Pinc, et al, “Effects of acid and alkaline based surface preparations on spray deposited cerium

based conversion coatings on Al 2024-T3”, Applied Surface Science, 255, 4061 (2009) representative of the types of characterization that were done.

5. Results and Discussion

5.1 Health and Safety Assessment

Boeing conducted an environmental, health, and safety assessment of the coating materials and systems being used on the project per the Hazardous Materials Identification System (HMIS), including the chromate materials used as controls. Shown in Table I below are the results of the assessment. The top two rows are for the two-layer CeCC and MUV coating system and the three lower rows are for the current chromate coating system. The assessment indicated that the materials used in the project are much more benign than the standard chromate system.

Table I - Health and Safety Assessment of Coating Materials

	Health (HMIS Rating)	Reactivity (HMIS Rating)	Flammability (HMIS Rating)	Carcinogenic (Cal. Prop. 65)	Teratogenic (Cal. Prop. 65)	SARA 313	VOC
Cerium Oxide	1	1	0	No	No	No	None
MUV	2	2	1	No	No	Yes	None
Chromate conv. coating	3	1	0	Yes	No	Yes	None
Epoxy chromate primer	3	1	3	Yes	No	Yes	334 g/l
Polyurethane topcoat	4	1	3	No	Yes	Yes	420 g/l

5.2 Cerium-based Conversion Coatings

The corrosion performance of CeCCs on high strength aluminum alloys was found to be dependent on many factors, especially the preparation of the surface prior to deposition, the solution chemistry of the deposition solution, and post-deposition treatment in phosphate solutions. Development of non-spray deposition methods were investigated for possible field application. Characterization of the coatings was done throughout the project to provide insight into coating formation that led to proposal of a deposition mechanism for CeCCs.

Surface Preparation

Alkaline Cleaning Temperature

Studies during the initial phase of the project investigated the influence of alkaline cleaning temperature on coating deposition and corrosion performance. The alkaline cleaner used, Turco 4215-NLCT from Henkel Corp., has a recommended operating range of 40-60°C. Prior work on Al 7075-T6 substrates had identified 55°C as the optimum cleaning temperature for immersion (dip) CeCCs. Since the focus of this project was on using a spray deposition process, a series of experiments was conducted to determine if a 55°C was the preferred alkaline cleaning temperature.

During spray deposition on Al 7075-T6 it was observed that the deposition rate was lower on panels cleaned at 45°C compared to panels that were cleaned at 55°C. After 20 sprays, the panels had changed color slightly, but only to a light orange, and the coatings were not as uniform as for a standard panel cleaned at 55°C. Therefore, more than 20 spray cycles were needed for panels cleaned at 45°C before the color of the panels changed from gray to a dark orange color. The panels cleaned at 55°C only required 20 spray cycles and they coated evenly and changed color as expected. The panels cleaned at 65°C changed color the fastest, but spraying continued for the standard number of 20 spray cycles over 15 minutes to ensure a thick coating. There was little to no measurable difference in the microstructures of the coatings examined using optical and electron microscopes. However, Auger depth profiling analysis indicated that the thickness of the cerium oxide layer increased from 100 nm for panels cleaned at 45°C, to 143 nm for panels cleaned at 55°C, and to 296 nm for panels cleaned at 65°C (Figure 2). Therefore, the color of the CeCC was a reasonable indication of coating thickness and could be used as process control parameter by operators in the field. Chemical surface analysis of the substrates after cleaning, but before CeCC deposition, did not reveal any significant differences in composition after using the different cleaning temperatures.

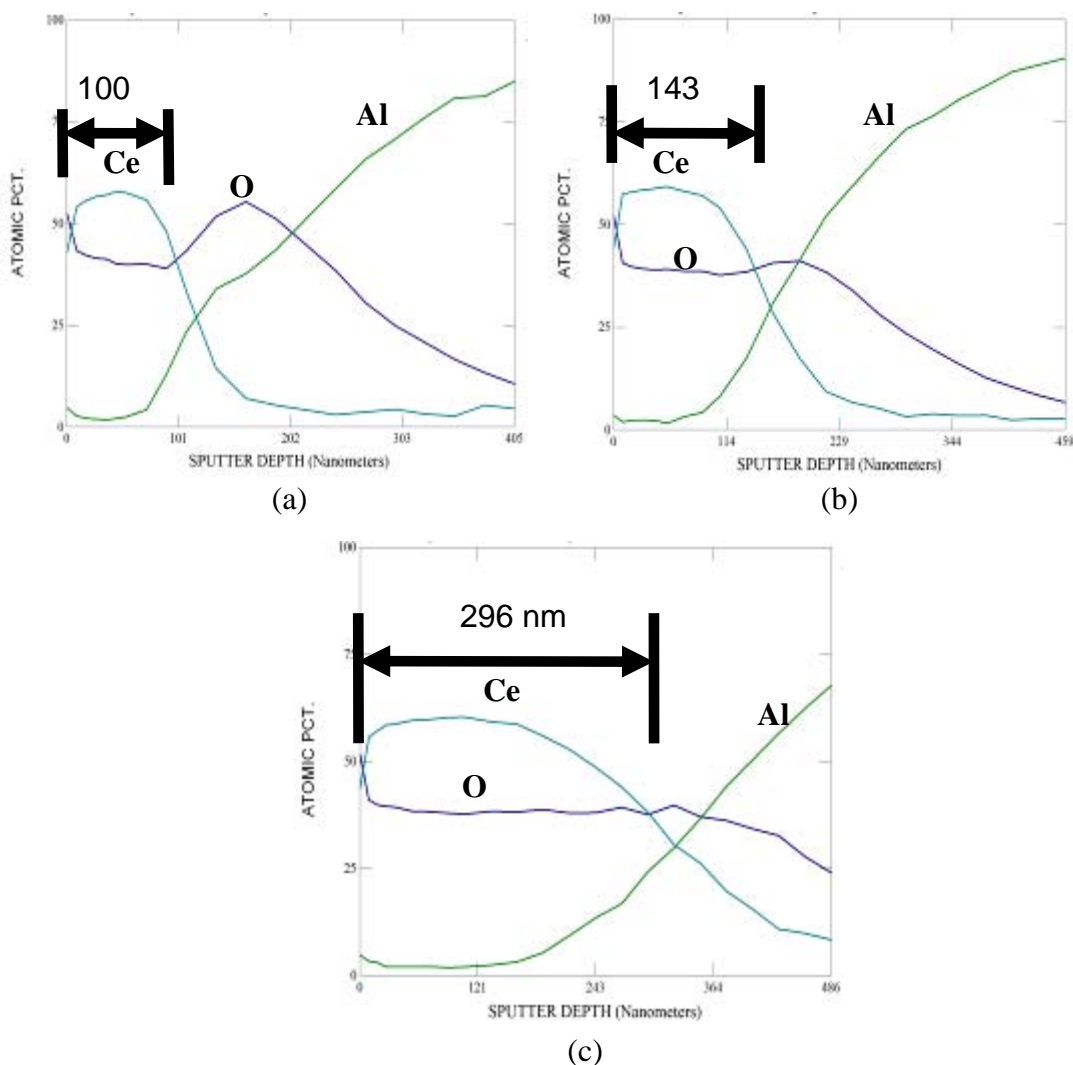


Figure 2. Auger Electron Spectroscopy depth profiles of spray coated samples on Al 7075-T6 cleaned at (a) 45°C, (b) 55°C, and (c) 65°C showing that the cerium oxide thickness increased with cleaning temperature.

Acid Activation

Standard cleaning procedures for 2024-T3 Al alloys initially used just an alkaline solution, Turco 4215 NCLT, prior to spray deposition. This resulted in a surface that was able to be evenly coated with ~300 nm of hydrated cerium oxide ($\text{CeO}_2 \cdot x\text{H}_2\text{O}$) after approximately 30 spray cycles. It is more desirable from a manufacturing standpoint to have fewer spray cycles so work was done to determine methods to decrease the number of spray cycles to obtain ~300-400 nm thick films with fewer spray cycles. It was determined that a 1 wt% sulfuric acid activation after an alkaline clean, but prior to deposition, on Al 2024-T3 reduced the number of spray cycles needed for a 400 nm thick film to five, with one spray cycle on acid activated panels resulting in a film ~275 nm in thickness. Shown in Figure 3 are a series of images from alkaline (only) cleaned Al 2024-T3 panels after a number of spray cycles while Figure 4 depicts an acid activated panel after just one spray cycle. It is clear from the images that very little coating

forms on the alkaline cleaned (only) panel up to ~10 spray cycles while a single spray cycle on acid activated substrates resulted in a fairly uniform coating.

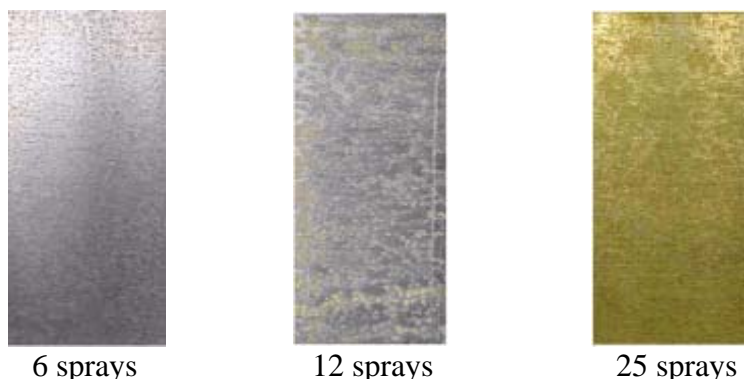
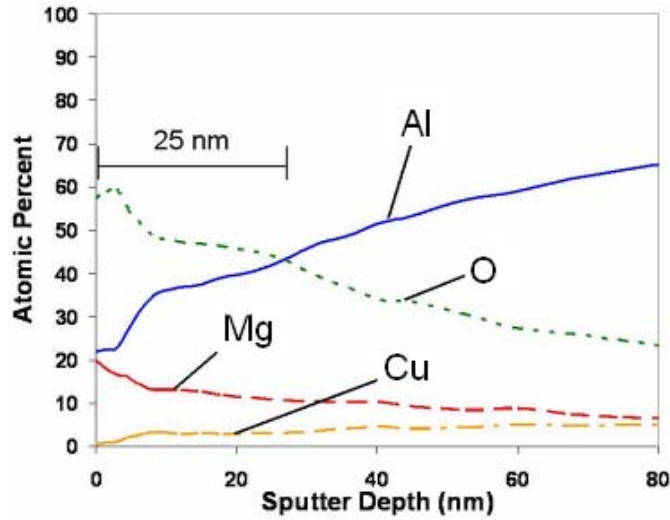


Figure 3. Optical images of alkaline cleaned Al 2024-T3 substrates after 6, 12, and 25 spray cycles.

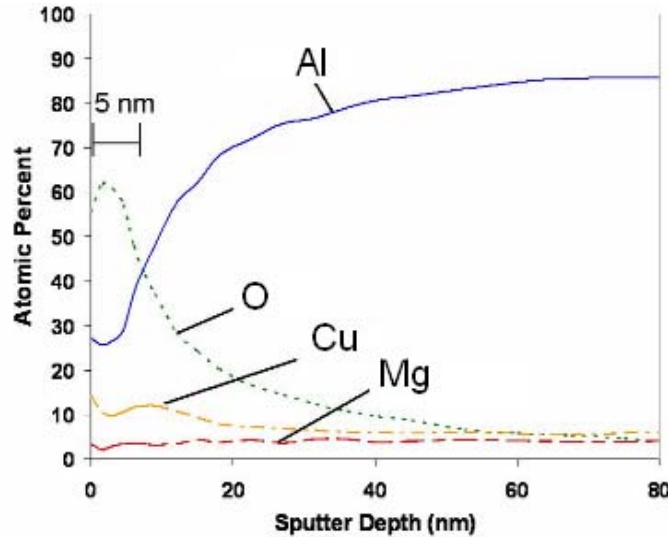


Figure 4. Optical images of an acid cleaned Al 2024-T3 substrates after 1 spray cycle.

In order to determine why the two cleaning processes produced such a dramatic difference in deposition rate, Auger electron spectroscopy (AES) was used to characterize the substrates after cleaning but prior to deposition. Shown in Figure 5 are AES depth profiles of Al 2024-T3 substrates after alkaline cleaning in Turco alkaline (Figure 5a) and activation in 1 wt% sulfuric acid (Figure 5b) solutions. The profiles show that the surface of the alkaline cleaned substrate had a significant amount of Mg and ~25 nm thick oxide film, along with little Cu. In contrast, the acid activated substrate surface had very little Mg, only a ~5 nm thick oxide, but ~10 at.% Cu after acid cleaning, which was an indication that the acid was more effective at removing the MgO/Al₂O₃ layer and exposing the underlying metal surface. The copper on the surface, most likely from intermetallic compounds in the alloy, acts as cathodic sites that facilitate precipitation of cerium oxide during deposition and increases the deposition rate. Concentrations of Cu and Mg in Figure 5 are different from the bulk values due to surface enrichment and depletion that occurs during heat treatment.



(a)



(b)

Figure 5. Auger depth profiles of Al 2024-T3 panels after (a) alkaline and (b) acid cleaning.

Alternative Surface Preparation Methods

The alkaline and acid cleaning described above was done by immersion of the panels in a beaker of solution. This method would not be feasible for field repair and touch ups on existing aircraft. During the final year of the program alternative methods to prepare surfaces for coating were studied, including hand application (wiping) of the cleaning solutions, ultrasonic agitation in water, and abrasive media (“sand”) blasting. These methods were compared to the standard immersion processes. After the alternative surface preparation techniques the aluminum surfaces were optically different from the unprepared surfaces and from each other. Immersion prepared and chemically wiped panels were both dark in color, but the immersion cleaned panels tended to be darker than the chemical wiped ones. Ultrasonically processed panels did not appear different than unprepared panels. Abrasively blasted panels had visibly rough surfaces that tended to be a brighter color than unprepared panels.

Electrochemically, treated Al 7075-T6 surfaces were more active than unprepared panels. Impedance scans (Figure 6) showed the blasted panels had the lowest charge transfer resistance ($3.4 \text{ k}\Omega\text{-cm}^2$) and that the ultrasonically cleaned panels had the highest charge transfer resistance ($5 \text{ k}\Omega\text{-cm}^2$). The tests found that all of the prepared panels had higher corrosion currents and lower charge transfer resistances than as-received panels and, therefore, had higher corrosion rates. Based on these results, the protective oxide layer was affected by the alternative surface preparation techniques.

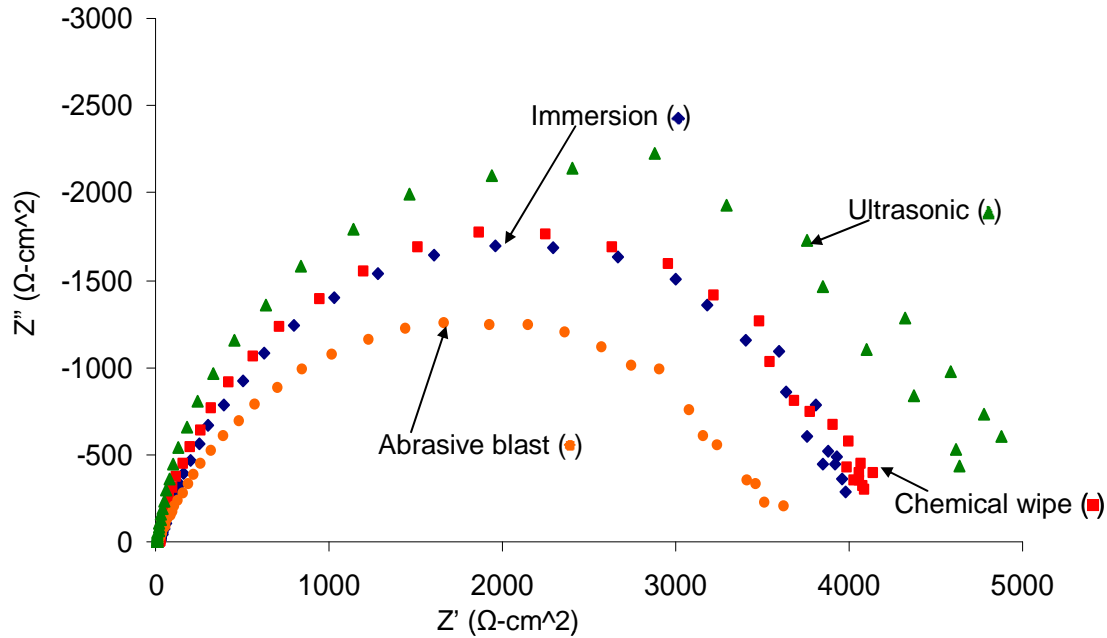


Figure 6. Nyquist plots for aluminum 7075-T6 panels prepared using different methods.

Electrochemical tests performed on alternatively prepared panels coated with CeCC found an increase in the measured corrosion resistance after coating. Results varied with the surface preparation used. Electrochemical impedance spectroscopy (EIS) tests found variation in charge transfer resistance values for panels with CeCCs, from about $5 \text{ k}\Omega\text{-cm}^2$ for the abrasively prepared coating to about $44 \text{ k}\Omega\text{-cm}^2$ for the immersion prepared coating (Figure 7). The charge transfer resistance values for panels with CeCCs were higher than the uncoated surfaces, but the immersion prepared and chemically wiped panels improved the most, consistent with the potentiodynamic scans. All of the coatings offered some protection compared to the prepared panels.

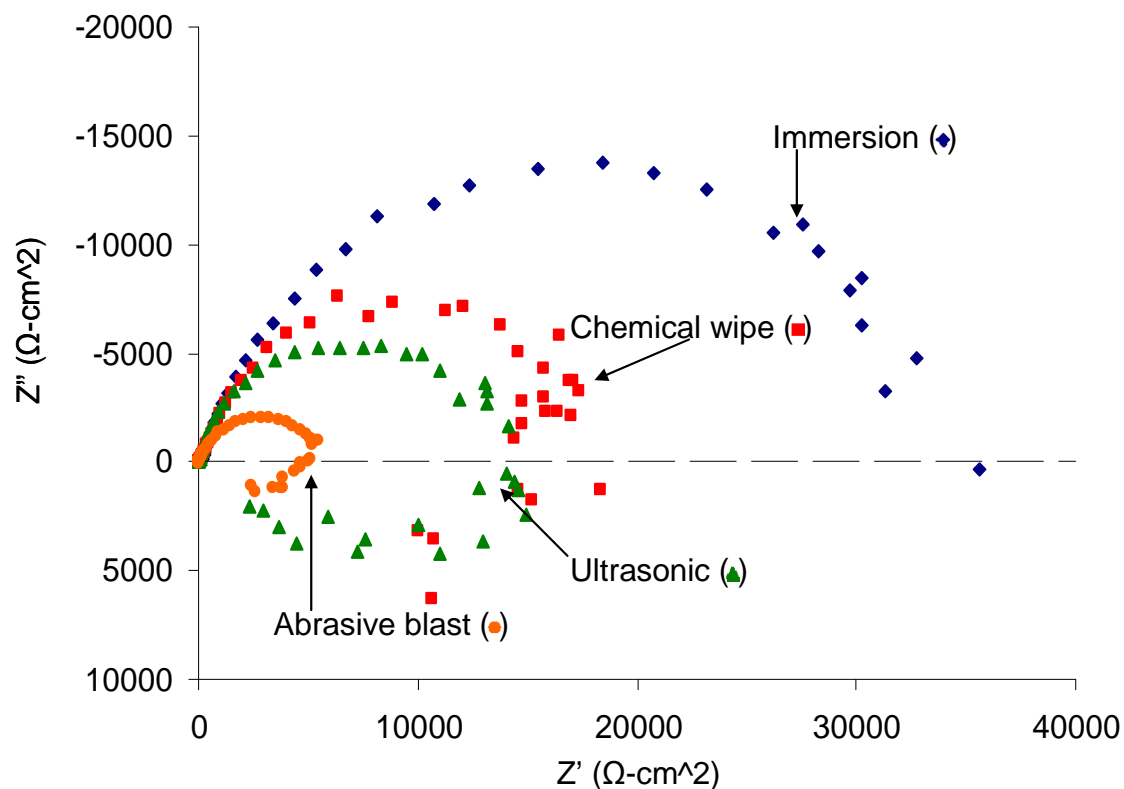


Figure 7. Nyquist plots for aluminum 7075-T6 panels with CeCCs deposited on panels prepared using each method.

Salt spray testing was also performed to compare corrosion performance of panels with CeCCs. Figure 8 contains images of the uncoated, prepared panels after 18 hours of exposure. The salt spray tests on the uncoated panels show the same trend as the electrochemical tests on the uncoated panels. The abrasively blasted panel corroded the most; it had a continuous layer of corrosion product on the surface. The immersion prepared panel had many large pits with tails, while the chemically wiped panel had fewer pits and smaller tails. The ultrasonically prepared panel had the fewest pits and the least amount of tailing of the prepared panels. Panels with CeCCs were less corroded than the uncoated panels (Figure 9). The salt spray results were consistent with the electrochemical tests on the coated panels. The most corroded panel was the blasted panel, again with a continuous corrosion product layer. The CeCC on the immersion prepared and chemically wiped panels performed the best in salt spray, with few pits and little tailing. The immersion pretreatment had slightly fewer pits. The ultrasonically prepared panel was the least corroded of the uncoated panels but the coating on the ultrasonically prepared panel did not protect as well as the coatings on the immersion prepared and the chemically wiped panels.



A



B



C



D

Figure 8. Optical images of prepared, uncoated aluminum 7075-T6 panels after exposure to salt fog for 18 hours A) chemical immersion, B) chemical wipe, C) ultrasonic processing, and D) abrasive blasting.



A



B



C



D

Figure 9. Optical images of coated aluminum 7075-T6 panels after exposure to salt fog for 18 hours A) chemical immersion, B) chemical wipe, C) ultrasonic processing, and D) abrasive blasting.

Deposition Conditions

pH, Ce and H₂O₂ Concentration Effects

Efforts to develop and optimize cerium oxide based conversion coatings on high strength aluminum alloy substrates focused on how the pH, cerium, and H₂O₂ concentration in the spray solution influenced coating formation and corrosion performance. The influence of pH (1.0-2.5), Ce concentration (1 to 4 wt.%), and H₂O₂ concentration (0 to 20 ml per 250 ml) on coating morphology, thickness, and corrosion performance after 5 spray cycles were investigated. It was found that the amount of Ce detected in the film by EDS in the SEM was ~30 wt% for all of the pH values evaluated but there were fewer cracks observed in the coating from pH 2.0 or 2.5 as compared to pH of 1.0 or 1.5 (Figure 10). As the concentration of Ce in the spray solution was increased from 1 to 4 wt.%, however, the amount of Ce detected on the surface by EDS increased from ~8 wt.% Ce in the film from the 1 wt.% Ce solution to ~30 wt.% Ce in the film for the 4 wt.% Ce solution (Figure 11), an indirect but reproducible method of evaluating coating thickness. As the coating thickness increased the corrosion resistance also improved up to 4 wt.% Ce in solution but then degraded beyond that point. Similarly, as the hydrogen peroxide concentration increased from 0 to 20 ml, the amount of Ce detected by EDS increased (Figure 12) with peroxide concentrations above 20 ml resulting in poorer corrosion performance.

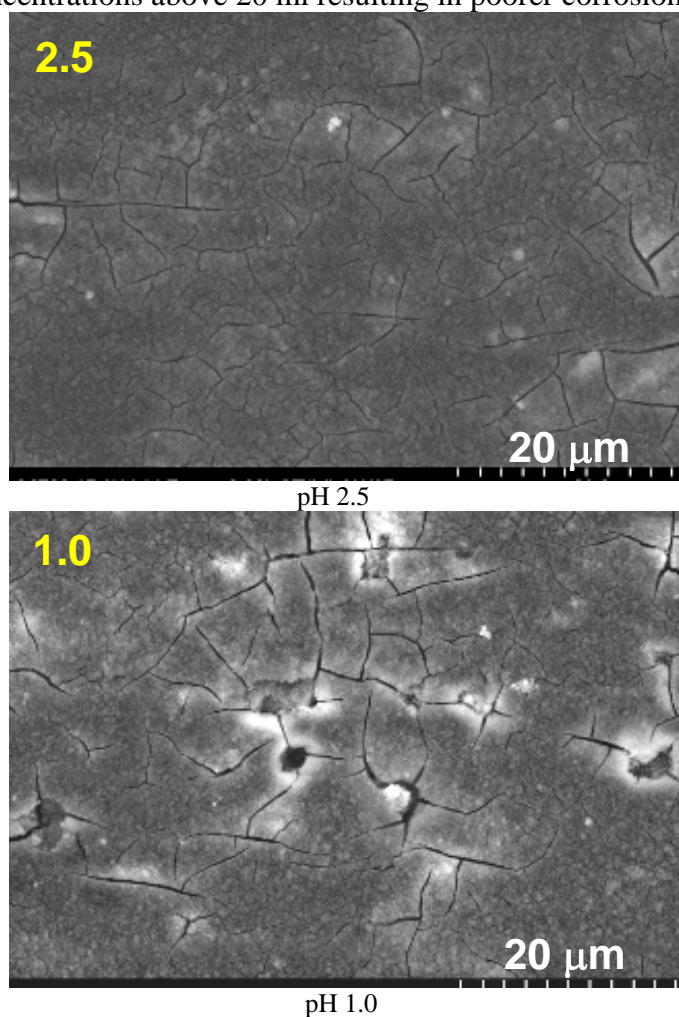


Figure 10. SEM micrographs of CeCC deposited using pH 1.0 and pH 2.5 spray solutions.

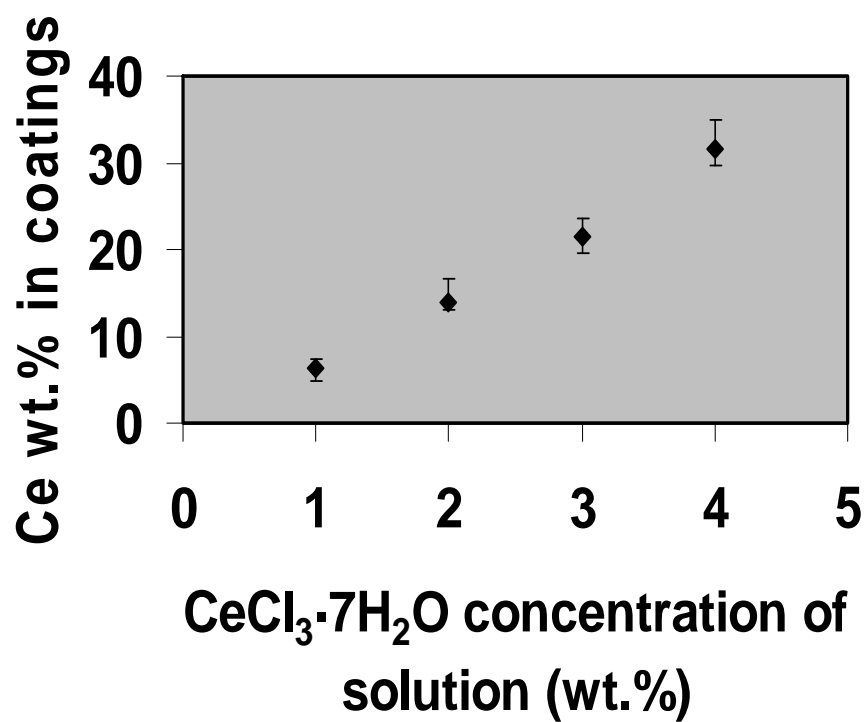


Figure 11. Plot of wt.% Ce detected by EDS vs. wt.% of Ce in the spray solution.

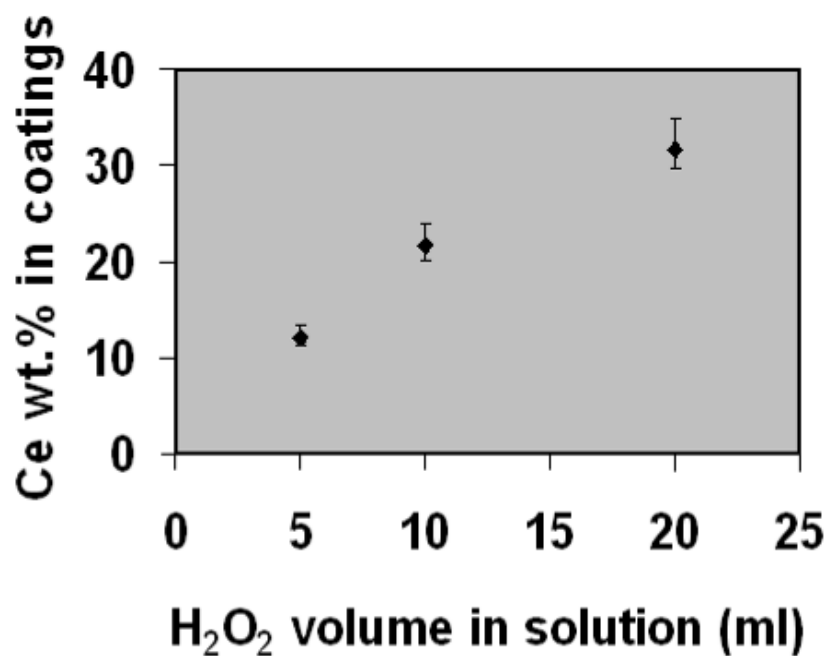


Figure 12. Plot of wt.% Ce detected by EDS vs. ml of H₂O₂ in the spray solution.

In a similar fashion, EIS measurements were made on CeCC panels in prohesion solution for up to 5 hours and the data indicated that the higher the impedance, or graphically the larger the loop and intercept value on a Nyquist plot, the better the performance during salt spray testing. Nyquist plots for Al 2024-T3 panels with CeCC after 3 hours in prohesion solution for coatings deposited with different concentrations of Ce (Figure 13) and H_2O_2 (Figure 14) indicated that as both the Ce and H_2O_2 concentration in the solution increased the impedance of the CeCC panel (which had been sealed in a phosphate solution) also increased. Note that no coating was deposited in the case of 0 ml of H_2O_2 since no oxidizer was present in the solution. The difference in pitting corrosion after five hours of EIS testing was also confirmed visually in that the higher the impedance, the better the corrosion resistance. Shown in Figure 15 are images of the peroxide test samples after 5 hours of EIS testing in prohesion solution.

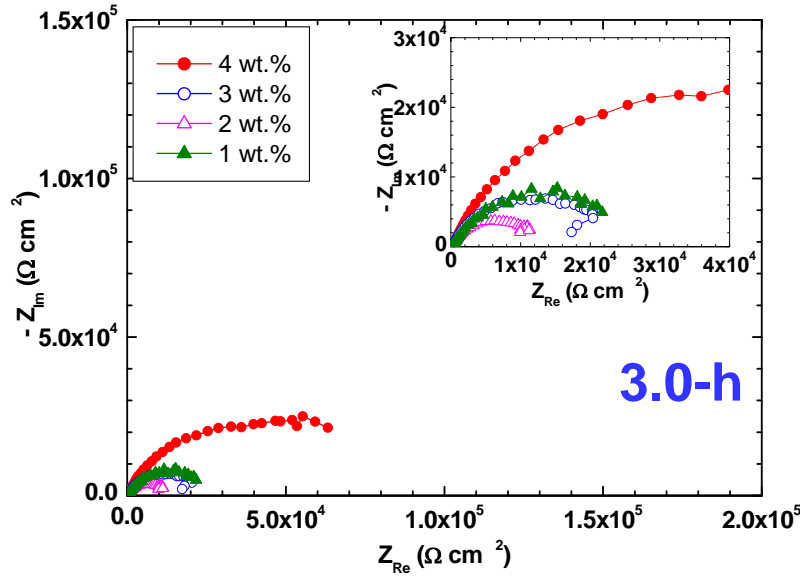


Figure 13. Nyquist plots of CeCC Al 2024-T3 panels in prohesion solution after 3 hours of testing for panels deposited using 1, 2, 3, and 4 wt.% Ce in the deposition solution.

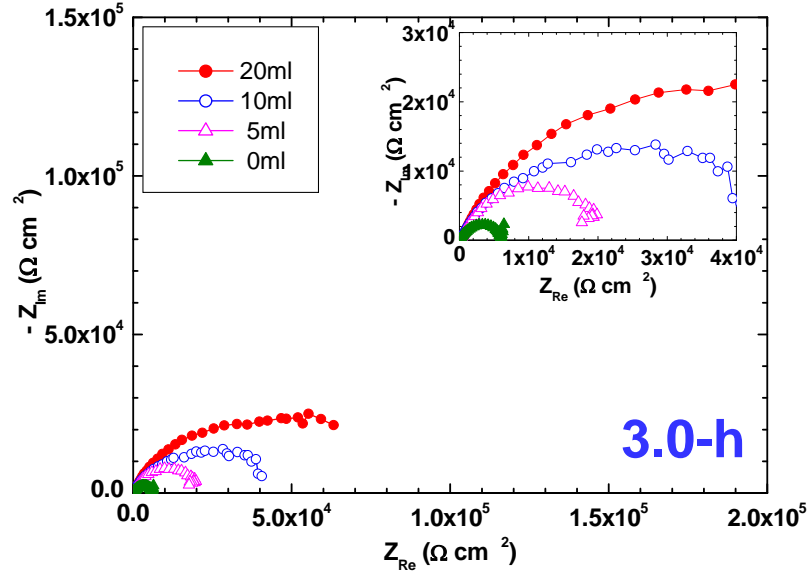


Figure 14. Nyquist plots of CeCC Al 2024-T3 panels in prohesion solution after 3 hours of testing for panels deposited using 0, 5, 10, and 20 ml of H_2O_2 in the deposition solution.

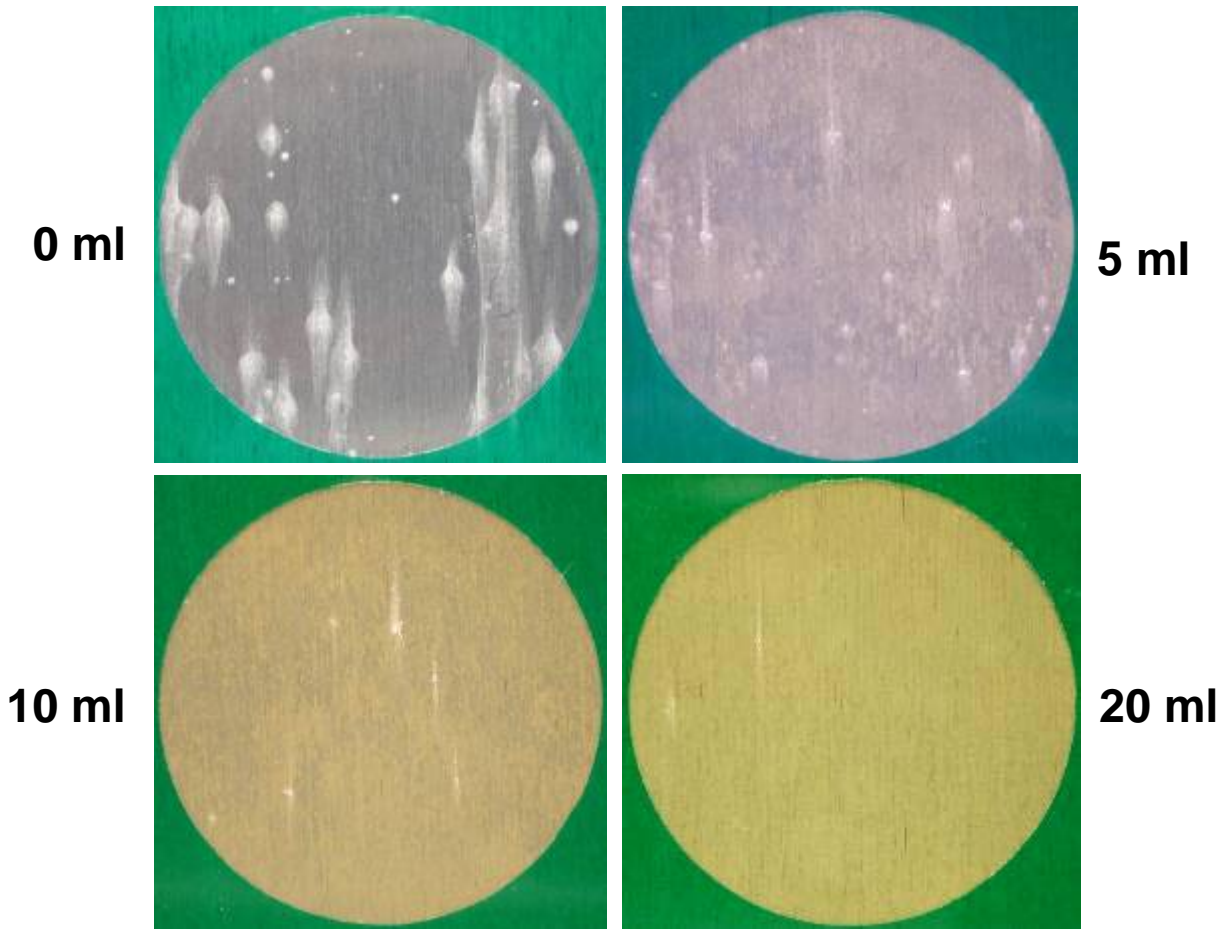


Figure 15. Images of CeCC Al 2024-T3 samples deposited using 0, 5, 10, and 20 ml of H_2O_2 in the spray solution following 5 hours of EIS testing in prohesion solution.

Gelatin Addition

The addition of a water soluble gelatin to the cerium-based conversion coating solution greatly improved the salt spray corrosion performance of the CeCC on high strength aluminum substrates that have been post-treated (those without post-treatment do poorly in salt spray regardless). Video recording of the deposition process had demonstrated that the presence of gelatin in the solution modifies the formation and stability of bubbles that form during the precipitation of cerium oxide that results in coating formation on the substrate surface. When gelatin is not present in the deposition solution the bubbles are unstable, readily forming and breaking; when gelatin is present the bubbles are very stable. If no gelatin is added to the deposition solution a CeCC with a lot of cracks and areas where the coating was no longer present, exposing the underlying substrate, was observed (Figure 16a). Coatings made without gelatin in the spray solution do very poorly during salt spray testing, with many pits and tails after just a few days (Figure 16b) regardless of any other changes in the overall process. Analysis of the films made without gelatin after 5 spray cycles using Auger depth profiling indicated that the coatings were ~850 nm thick (Figure 17). Many ceramic thin films exhibit cracking and loss of adhesion at thicknesses approaching 1000 nm. In contrast, CeCCs deposited with gelatin in the spray solution had very few to no cracks or uncoated areas (Figure 18a) and performed well during salt spray testing (Figure 18b). The thickness of films made with gelatin after 5 spray cycles was typically in the 350-400 nm range (Figure 19), meaning that the deposition rate is significantly lower when gelatin is present in the spray solution.

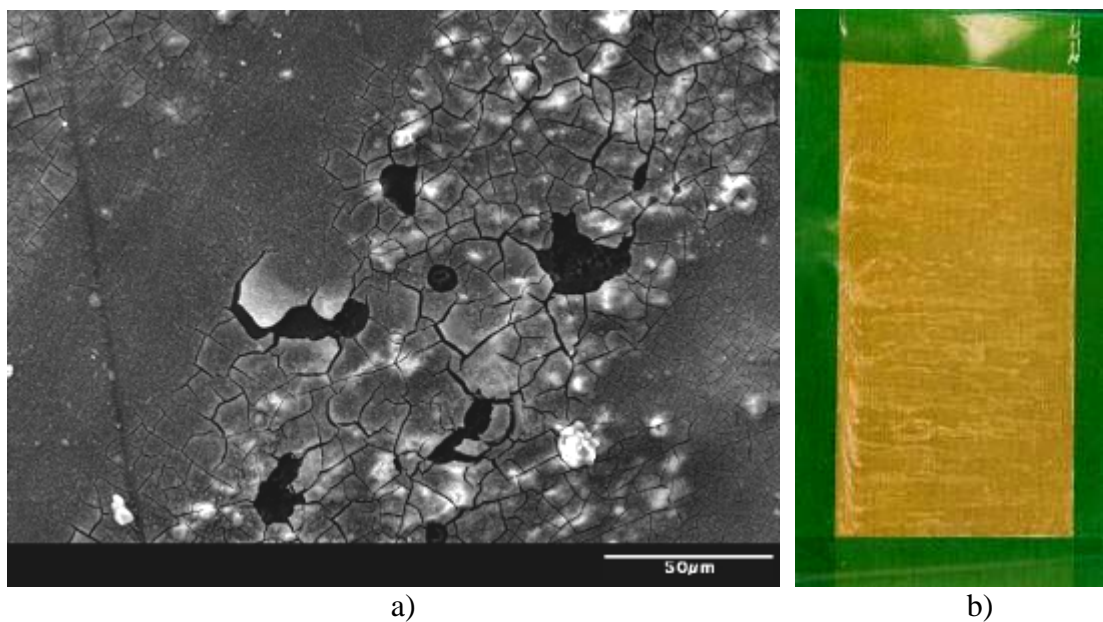


Figure 16. a) Scanning electron micrograph of a CeCC deposited on an Al 2024-T3 panel with no gelatin in the spray solution; b) optical image of panel after 2 days of salt spray testing.

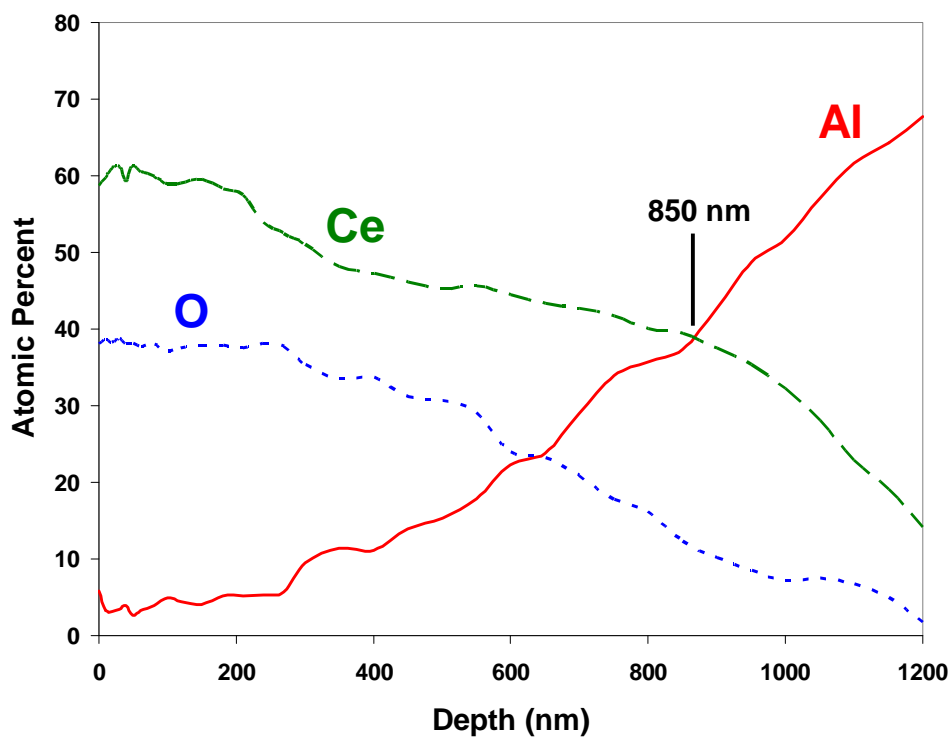


Figure 17. Auger depth profile of a 5 spray cycle CeCC deposited on an Al 2024-T3 panel with no gelatin in the spray solution.

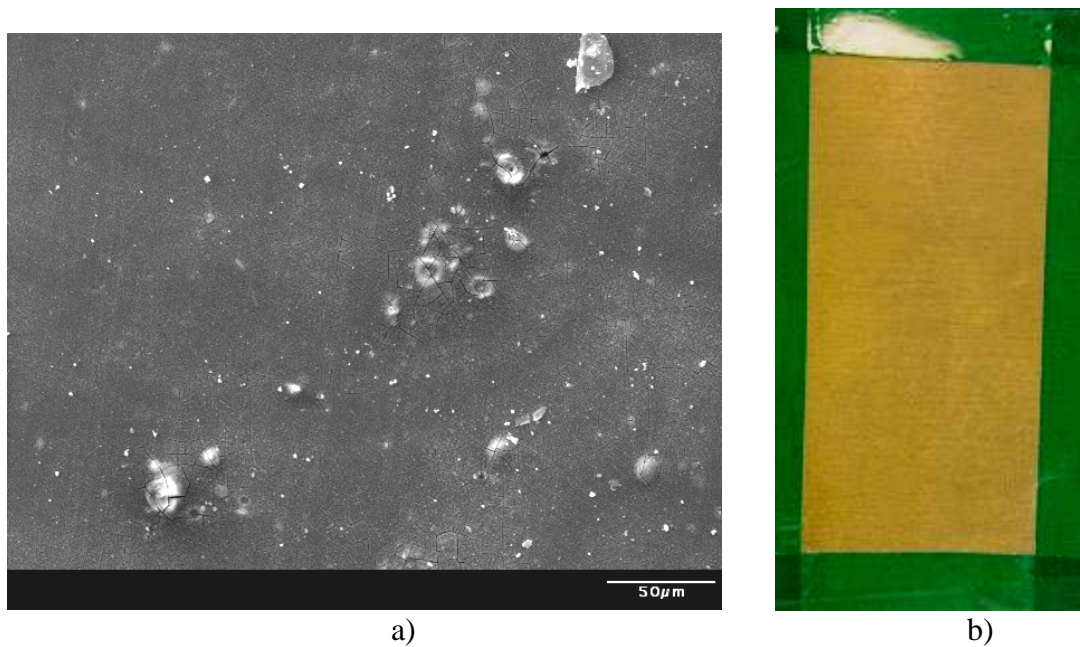


Figure 18. a) Scanning electron micrograph of a CeCC deposited on an Al 2024-T3 panel with 3200 ppm gelatin in the spray solution; b) optical image of panel after 7 days of salt spray testing.

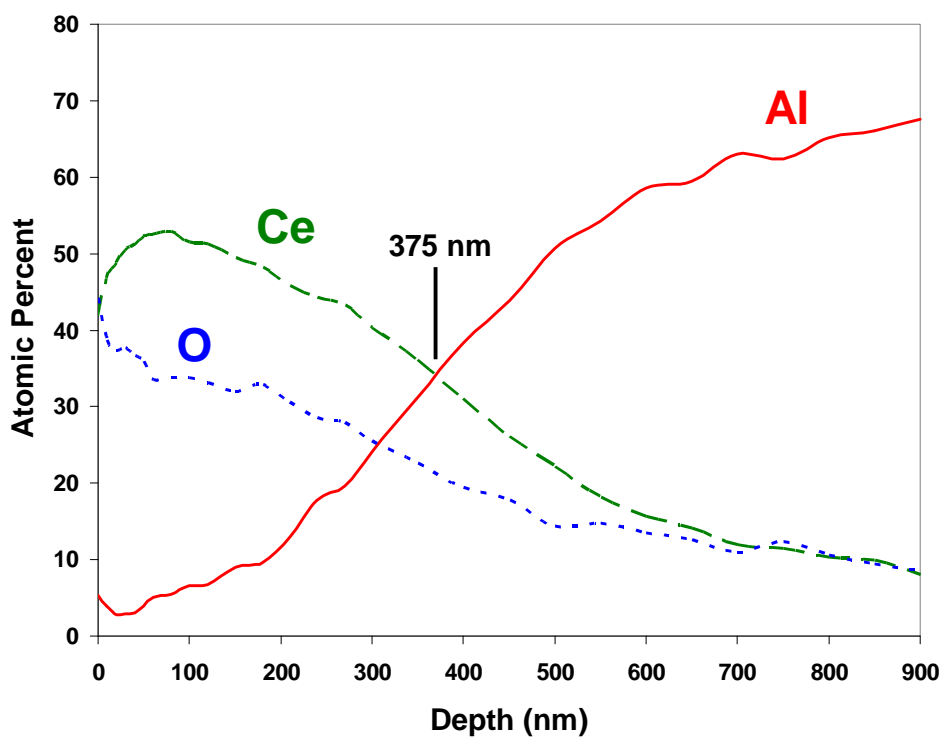


Figure 19. Auger depth profile of a 5 spray cycle CeCC deposited on an Al 2024-T3 panel with 3200 ppm gelatin in the spray solution.

Electrochemical impedance characterization of films made without (0 ppm) and with 3200 ppm of gelatin in solution indicated that the impedance of the CeCC was significantly higher for the films made with gelatin ($>100 \text{ k}\Omega\text{-cm}^2$) than those without gelatin ($\sim 50 \text{ k}\Omega\text{-cm}^2$, Figure 20). This correlated very well with the corrosion testing, as films with higher impedance performed better during salt spray exposure.

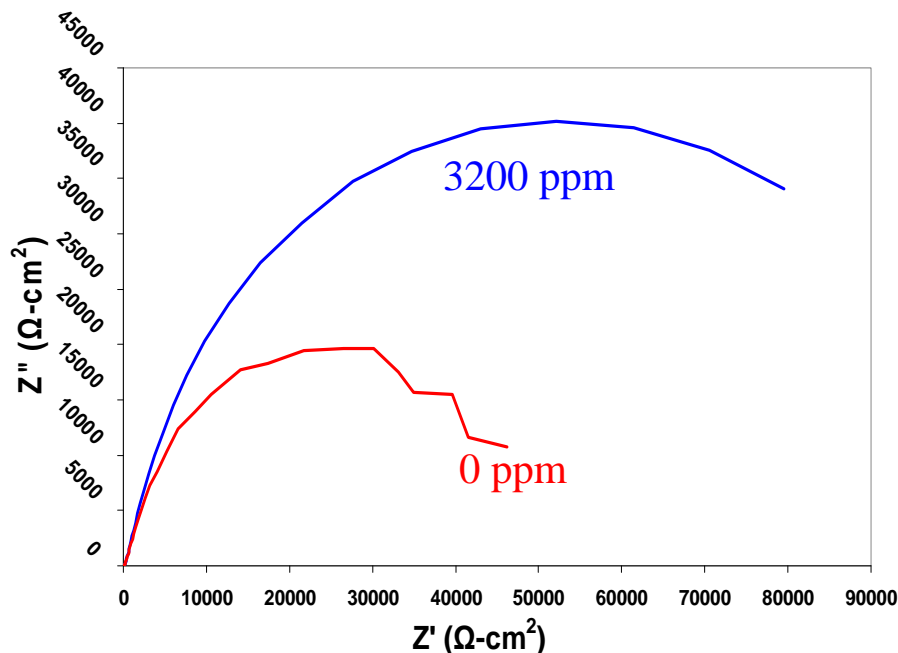


Figure 20. Electrochemical impedance of CeCC deposited on an Al 2024-T3 panel with 3200 ppm and no gelatin (0 ppm) in the spray solution.

Post-Treatment

The formation of cerium phosphate during post treatment greatly improves the corrosion protection of CeCCs on Al substrate. Investigations to determine the influence of post treatment parameters on corrosion performance were conducted to understand the improvement. The initial study focused on the use of different phosphate sources for the post treatment solution. Included in the study were orthophosphates (PO_4), pyrophosphates (P_2O_7), and polyphosphates (P_3O_{10}), along with as deposited (unsealed) CeCCs for comparison. SEM and optical images of specimens that were as deposited and post treated in a PO_4 solution (Figure 21), and post treated in a P_2O_7 solution (Figure 22) indicate the differences possible using different phosphate sources. It was determined that the PO_4 based solutions had the fewest cracks in the films, performed the best in salt spray, and had the highest electrochemical impedance values (Figure 23). The presence of a hydrated CePO_4 phase after post treatment (Figure 24) correlated strongly with good corrosion performance during salt spray testing.

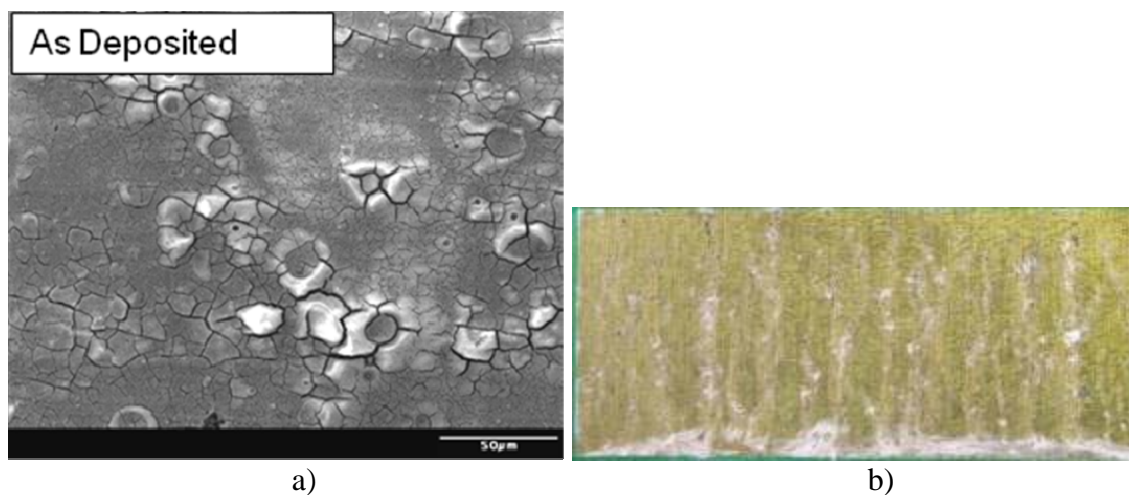


Figure 21. a) Scanning electron micrograph of an as deposited (unsealed) CeCC on an Al 2024-T3 panel; b) optical image of panel after 14 days of salt spray testing.

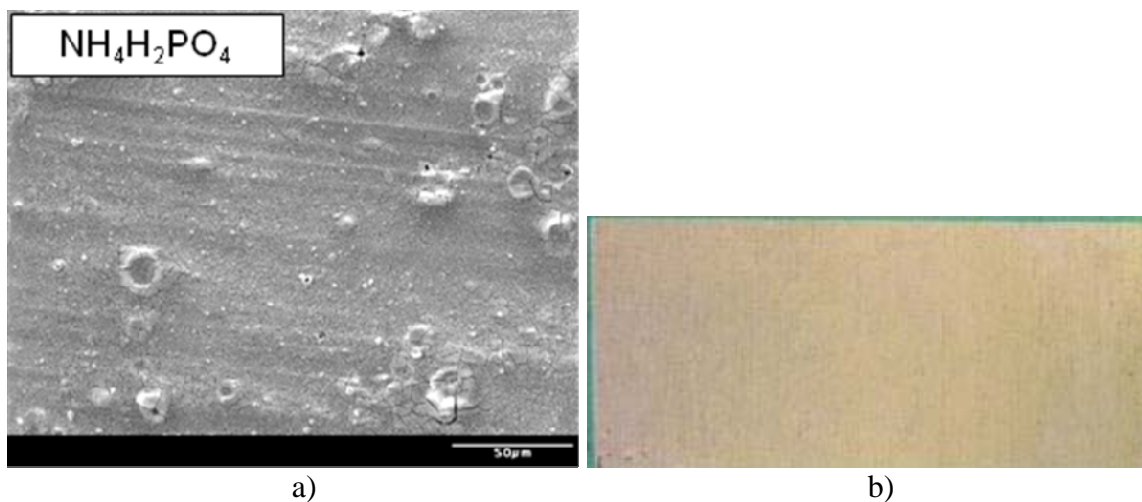


Figure 22. a) Scanning electron micrograph of a CeCC post treated in a $\text{NH}_4\text{H}_2\text{PO}_4$ solution at 85°C for 5 minutes on an Al 2024-T3 panel; b) optical image of panel after 14 days of salt spray testing.

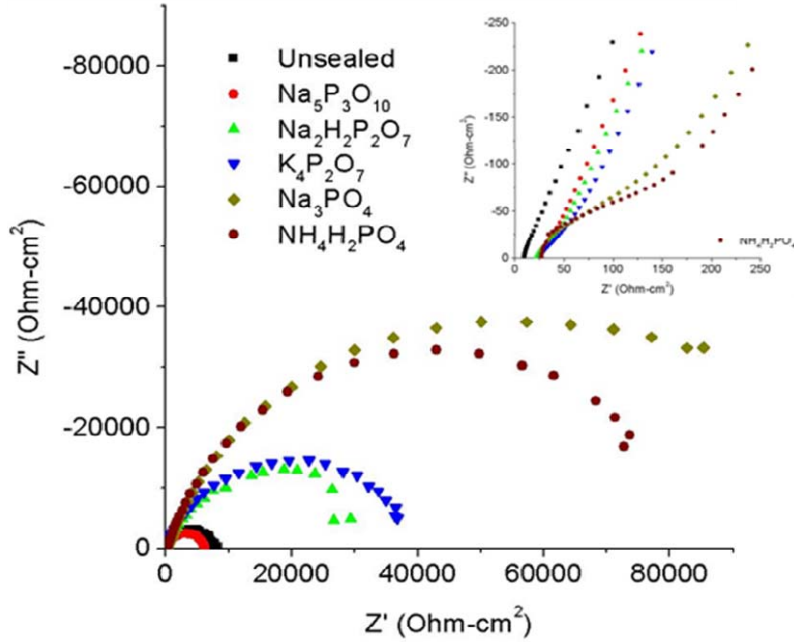


Figure 23. Electrochemical impedance of CeCCs on Al 2024-T3 panels post treated in different phosphate solutions.

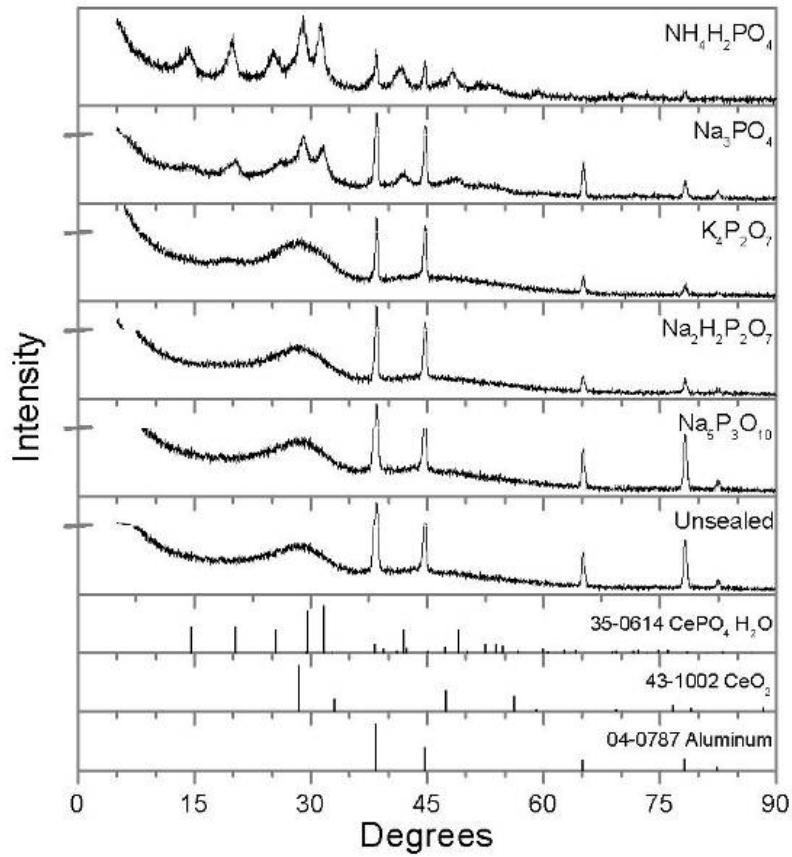


Figure 24. X-ray diffraction patterns of CeCCs post treated in different phosphate solutions, and one not post treated (unsealed), on Al 2024-T3 panels.

A summary of the phosphate sealing studies is presented in Table II. Corrosion performance was qualitatively evaluated by assigning a ranking to each condition. In Table II 5 dots corresponds to passing 2 weeks of ASTM B117 salt spray testing, 3 dots corresponds to passing 1 week of ASTM B117, and 1 dot is failure after 1 day of salt spray testing; 2 and 4 dots correspond to conditions that fall between those values. The electrochemical testing of the panels correlated very well with the other characterization methods. In general, higher charge transfer resistance, R_{ct} , lower corrosion current density, i_{corr} , and more positive pitting potentials, E_{pit} , were associated with panels that were found to have formed $CePO_4$, had fine cracks, and performed best during salt spray testing.

Table II - Summary of CeCC Phosphate Sealing Study

	Conditions	R_{ct} (k Ω -cm ²)	i_{corr} (μ A/cm ²)	E_{pit} (mV)	CePO ₄ Formed	Morphology (Cracks)	Corrosion Performance
	Unsealed	8	1.50	-435	No	Large	••
Source	NH₄H₂PO₄ (2.5 wt%)	60	0.60	-261	Yes	Fine	•••••
	Na₃PO₄ (2.5 wt%)	51	0.45	-280	Yes	Fine	•••••
	K₄P₂O₇ (2.5 wt%)	25	0.74	-275	No	Fine	••••
	Na₂H₂P₂O₇ (2.5 wt%)	15	1.17	-322	No	Defects	•••
	Na₅P₃O₁₀ (2.5 wt%)	4	2.14	-343	No	Defects	•
Time	10 sec (85 °C)	17	1.41	-401	No	Large	••
	30 sec (85 °C)	25	1.98	-340	No	Fine	•••
	2 min (85 °C)	52	0.84	-329	Yes	Fine	••••
	10 min (85 °C)	62	1.00	-245	Yes	Fine	•••••
Temp.	55 °C (5 min)	49	0.83	-384	No	Large	••
	70 °C (5 min)	63	0.66	-320	Yes	Fine	••••
	85 °C (5 min)	91	0.65	-258	Yes	Fine	•••••

Deposition Methods

Brush Application

During the last year of the project, work was done to determine the feasibility of depositing a CeCC onto Al 2024-T3 substrates using a standard paint brush application. This process could be used for field repairs and other locations where a spray booth, immersion tank, or electrolytic bath were not available. The same solution was used to deposit CeCCs by spray and brush methods in order to compare the application methods. Using similar substrate cleaning processes, it was found that a uniform CeCC could be deposited using either a spray or brush application method. The brush samples were done by immersing the paint brush into the CeCC sample and swabbing it across the surface for a few seconds, waiting ~30 seconds, and re-applying CeCC solution with the brush up to 7 times. In all cases it was possible to obtain a CeCC using a brush application method. A plot of spray and brush applied CeCC thicknesses as a function of deposition cycles is presented in Figure 25. The spray application resulted in a thicker coating per deposition cycle than the brush application but the thicknesses were in the range of ~250 to 400 nm that had previously been demonstrated to provide corrosion protection during salt spray testing.

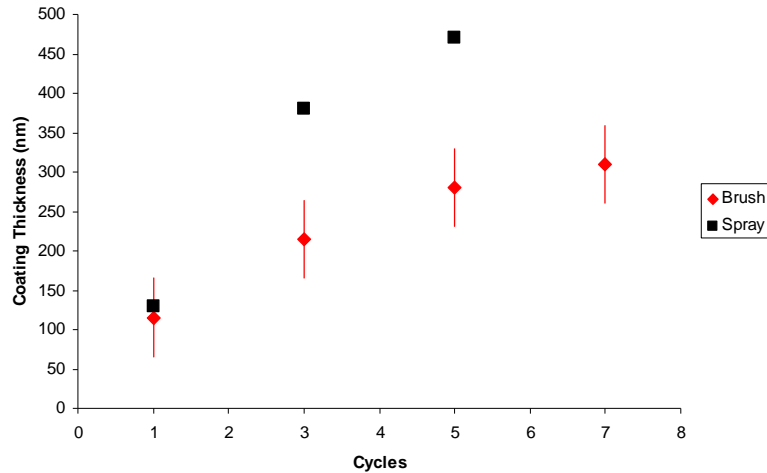


Figure 25. Coating thickness as a function of the number of brush or spray deposition cycles.

X-ray diffraction analysis of brush and spray applied CeCCs coatings after post treatment indicated that the 3, 5, and 7 deposition cycle brush coatings did not have peaks associated with hydrated CePO_4 as compared to the spray 3 and 5 cycle samples that did have CePO_4 peaks (Figure 26). Corrosion performance of brush panels during salt spray testing was similar to, but not quite as good as, the spray panels. It was not determined why the brush deposited CeCCs did not transform into CePO_4 during post treatment but does reinforce the importance of deposition conditions on the structure and performance of cerium-based corrosion coatings.

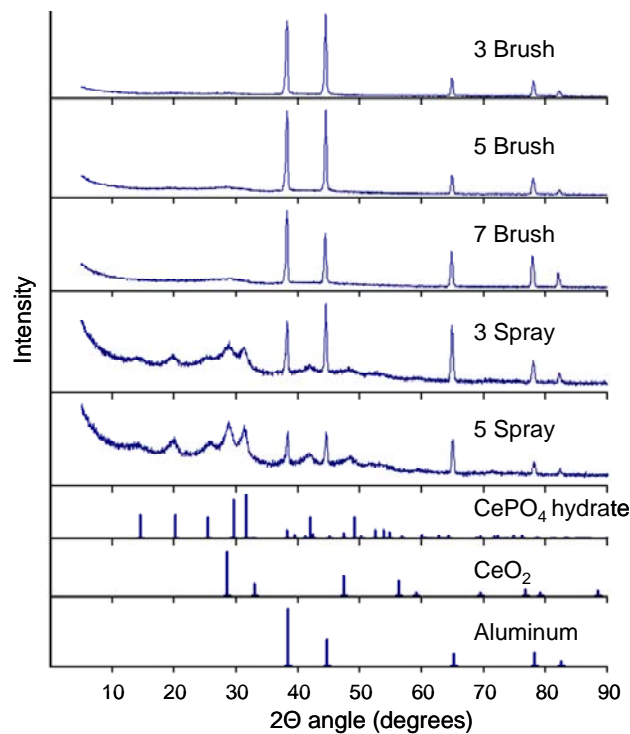


Figure 26. XRD spectra for coatings deposited using three, five, and seven brush cycles, and three and five spray cycles.

Deposition Mechanism

Based on all of the data available and experimental observations, a mechanism describing what is thought to occur during deposition (precipitation) of CeCCs on high strength Al alloys was developed. Although it can't be shown interactively in this document as it is a step-wise mechanism, the two major components of the mechanism are shown in Figures 27 and 28. Figure 27 shows an increase in pH associated with electrochemical reactions involving the alloy substrate that contains cathodic (intermetallic compounds) and anodic (Al matrix) sites. Reactions that increase the pH of the solution near the Al/solution interface drive the precipitation reactions, including peroxide decomposition, generation of water, and consumption of H^+ . The actual precipitation reactions in the region of higher pH (> 4.5) can involve cerium hydroxide or peroxide species depending on the local conditions (Figure 28). In either case these can decompose into hydrated cerium oxide or cerium hydroxide phases. The corrosion performance of the films is much better after phosphate post treatment ("sealing"), so conversion into phosphates is usually done. Whether or not the cerium oxide/peroxide species present after deposition can affect the phosphating process is not fully understood and requires more study.

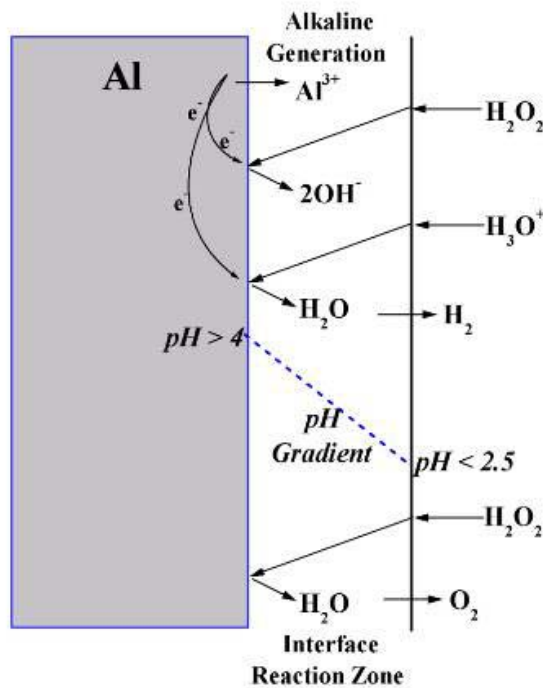


Figure 27. Schematic drawing of reactions that increase the pH near the surface of Al substrates that causes cerium precipitation from solution.

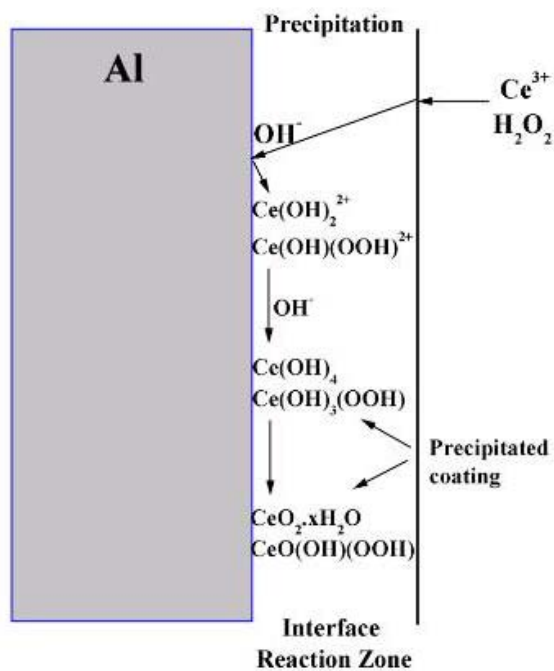


Figure 28. Schematic drawing of reactions that occur during CeCC precipitation from solution.

Characterization

Sub-Surface Crevices

During calendar year 2008 Missouri S&T installed and began operation of a FEI Nanolab 600 focused ion beam (FIB) scanning electron microscope. The FIB is able to selectively remove material from specific sites on a sample, enabling cross sectional views at and just below the surface of the specimen. Shown in Figure 29 is a low magnification image of a sample after removing ~20 μm long, ~10 μm deep section from a CeCC on an Al 2024-T3 substrate (essentially looking down into a hole dug out from the surface). Shown in Figure 30 is a cross section image of an Al 2024-T3 panel after acid activation cleaning, with no CeCC present. The figure shows that the Al 2024 substrate is continuous and without any sub-surface damage prior to CeCC deposition.

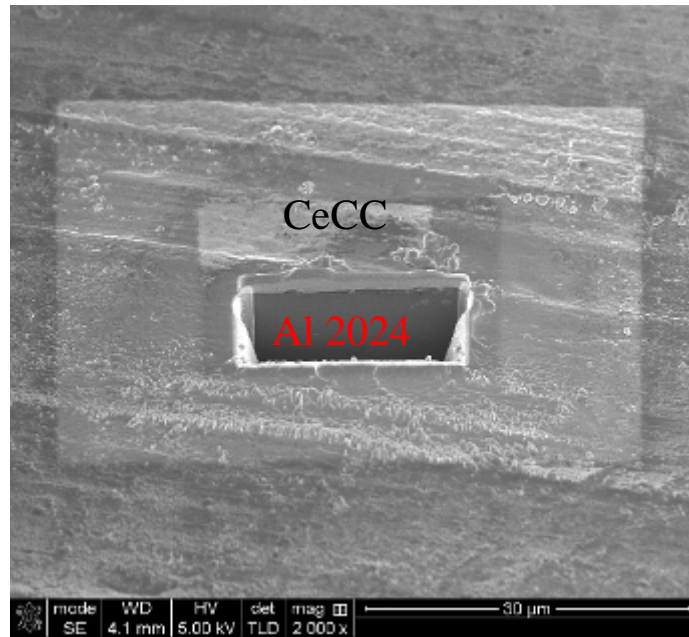


Figure 29. Electron micrograph image of a CeCC on an Al 2024-T3 panel after FIB sectioning.

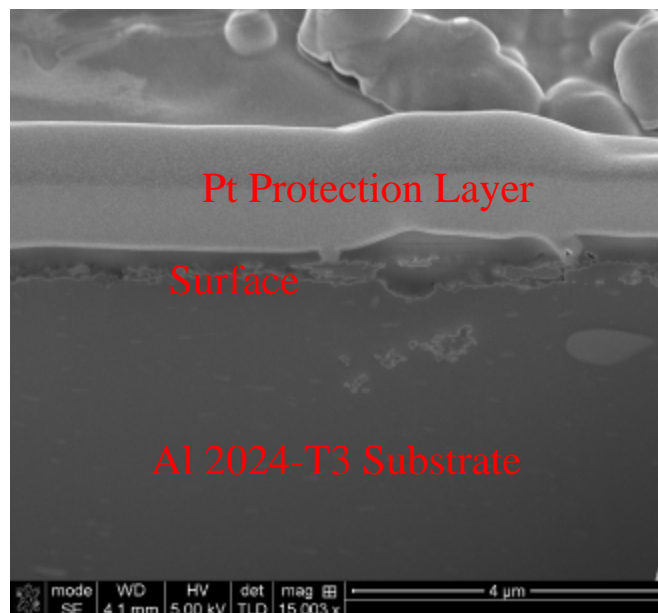


Figure 30. Cross sectional micrograph image of an Al 2024-T3 panel after acid activation cleaning (no sub-surface crevices).

Presented in Figure 31 is a FIB cross sectional image of samples after spray deposition of CeCC onto cleaned Al 2024-T3 substrates. The areas examined were near the large cracks in the CeCC, ~10% of the total surface area on a sample (90% have fine or small cracks). It was observed that the Al 2024-T3 substrate under the CeCC with large cracks had sub-surface crevices, an indication that the Al substrate had been preferentially etched and material removed during deposition. The crevices can be near the surface only or extend down into the substrate

several micrometers. It should be noted that the areas with fine cracks (90% of total surface area) do not have the sub-surface crevices and look similar to Figure 30.

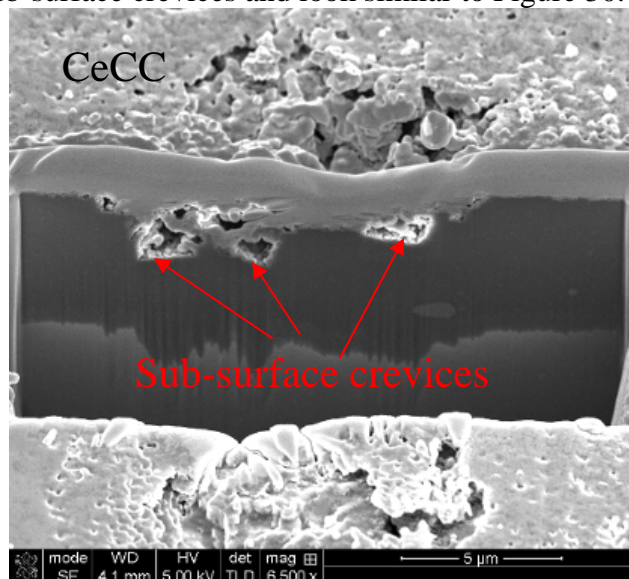


Figure 31. Cross sectional micrograph image of an Al 2024-T3 panel after CeCC deposition (contains sub-surface crevices).

To investigate the origin of the sub-surface crevices a solution consisting of H_2O_2 and NaCl was made to simulate the H_2O_2 plus CeCl_3 solution used to deposit CeCCs. Without the presence of Ce in the solution there is no film deposited but the active etching species, Cl^- and H_2O_2 , are still present. As seen in Figure 32 below, the sub-surface crevices were observed after spraying the salt plus peroxide solution on the surface of a cleaned Al 2024-T3 panel. Therefore, the concentration of the chloride and hydrogen peroxide in the CeCC spray solution is sufficient to preferentially etch the Al 2024-T3 substrate. Studies were conducted that demonstrated the reducing the amount of Cl^- and H_2O_2 in the deposition solution reduced, or eliminated, the formation of sub-surface crevices. However, samples without sub-surface crevices did not perform well during corrosion testing.

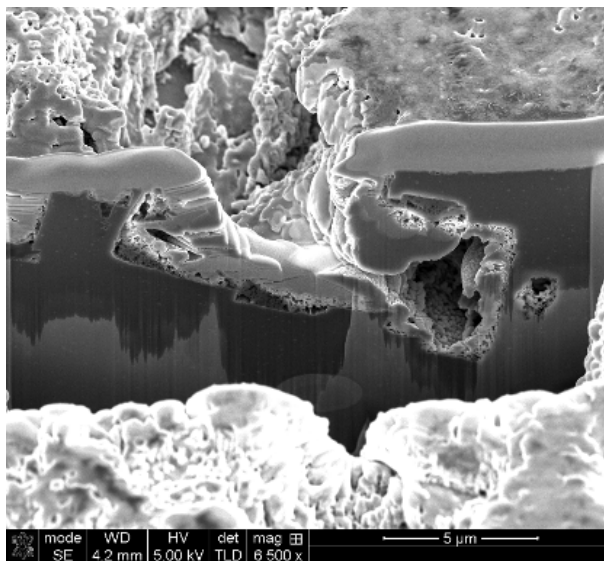
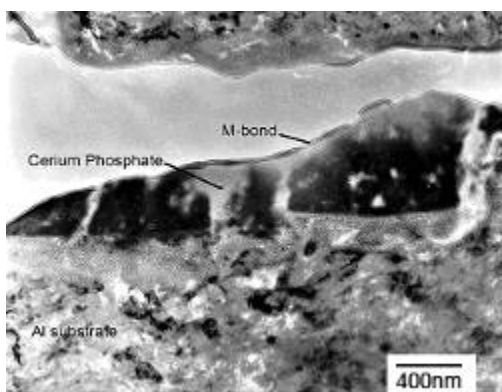


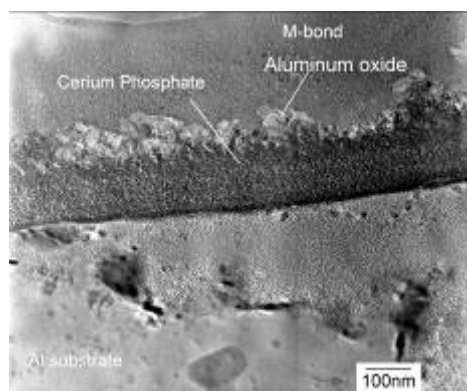
Figure 32. Cross sectional micrograph image of an Al 2024-T3 panel after spraying a H_2O_2 + NaCl solution on the surface.

Post Salt Spray Surface Analysis

Characterization of CeCC panels before and after salt spray testing was done throughout the project. Panels that passed the 14 day visual inspection criteria after salt spray testing were analyzed to see if differences in material composition or structure could be measured. Cross sectional transmission electron microscopy (TEM) of the phosphate sealed CeCC coating before salt spray exposure indicated that the film was a dense, continuous coating that was a few hundred nanometers in thickness (Figure 33a). After 14 days in the salt spray cabinet the CeCC was still present but an additional layer was present on the surface of the CeCC (Figure 33b). Additional analysis of the panels using depth profiling revealed that the CeCC before salt spray testing was a mixture of Ce, O, and P (Figure 34a) but after salt spray exposure Al and O were present on top of the CeCC (Figure 34b). The presence of an oxide layer on top of the CeCC after salt spray testing was detected on multiple samples throughout the project. Collectively, the TEM and AES results show that an aluminum oxide layer was present on the surface of the CeCC after 14 days of salt spray exposure on panels that passed 336 hours of testing.

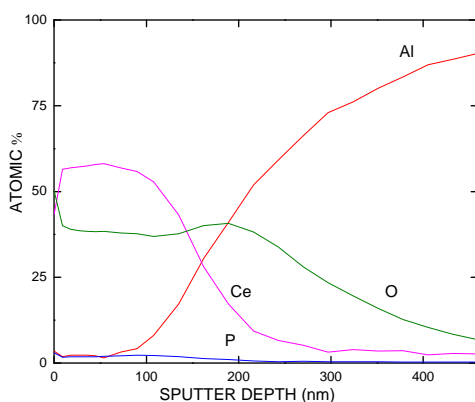


a)

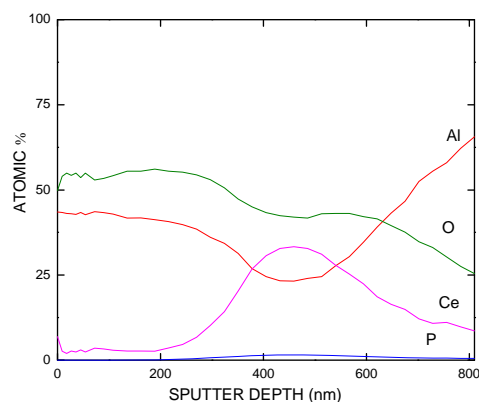


b)

Figure 33. Cross-sectional TEM images of cerium based conversion coatings: a) as-deposited, b) after 14 days of salt spray testing.



a)



b)

Figure 34. Auger electron spectroscopy depth profiles of cerium based conversion coatings: a) as-deposited and b) after 14 days of salt spray testing.

5.3 Multifunctional UV (MUV) Curable Coatings

Development and evaluation of MUV coatings was done throughout the project. A total of 5 rounds of experimental testing were conducted. Within the first few months of the project it was decided that each round of testing would use commercially available chromate and non-chromate coatings as controls. This was done in order to compare results from military approved coatings to the ones being developed and tested in this project. A brief overview of the 5 rounds (rds) of testing is presented in Table III. The detailed results from the testing are available from the project Principal Investigator.

Table III - Summary of MUV Testing

- Completed 5 Rounds of MUV Test and Evaluation on A1 2024 and A1 7075 Substrates
 - Chromate & Non-Chromate Controls As Reference (CrCC/TCP, Epoxy Primer, Polyurethane Top Coat)
 - MUV on CrCC, CeCC, TCP and Bare A1 2024-T3
 - B117 Salt Spray, SO₂ Exposure, Filiform, Cross Hatch Adhesion, Skydrol Resistance, GE Impact, Low Temp Mandrel, Accelerated UV Weathering
- Rd 1 (FY06) – Drawbar MUV, 2 Corrosion Inhibitors Evaluated
- Rd 2 (FY07) – Drawbar MUV, 3 Corrosion Inhibitors Evaluated
- Rd 3 (FY08) – Spray MUV, Wayne Pigment Inhibitor
- Rd 4 (FY08/09) – Spray MUV, Wayne, Different Formulations
 - Also Evaluated Gloss White
- Rd 5 (FY09) – Spray MUV, Wayne, Flexibility Adjustments

Round 1 MUV Evaluations

Round 1 testing was limited to salt spray testing only of MUV coatings with Hybricor 204 or Deft corrosion inhibitor on chromate and cerium coated Al 2024-T3 or Al 7075-T6 panels. Commercial chromate and non-chromate coating were used as controls. The controls were spray applied at Boeing and the MUV coatings were drawbar applied at LCC. The MUV coatings with Hybricor 204 inhibitor performed as well as or better than the controls in terms of preventing salting in the scribe after 3000 hours of testing. Shown in Figure 35 are some of the panels after 3000 hours testing, with the Hybricor 204 MUV coated panels on CrCC and CeCC having no visible salting in the scribe. This result was very significant as it demonstrated that a UV curable formulation loaded with corrosion inhibitors has the capability of protecting against corrosion of scribed high strength aluminum panels on chromate and non-chromate conversion coatings.



Chromate Control



Non-Chromate Control



Deft MUV on CrCC



Deft MUV on CeCC



Hybricor 204 MUV on CrCC



Hybricor 204 MUV on CeCC

Figure 35. Optical images of Stage 1 Al 2024-T3 coated panels after 3000 hours of neutral salt spray testing.

The MUV coatings were stripped off some of the panels following 3000 hours of salt spray testing to determine if corrosion under the coating had occurred. As shown in Figure 36 the surface and scribe of the Al had no visible corrosion or staining for the Hybricor 204 panels while the Deft MUV and control panels each had corrosion by-product in and around the scribe.



Chromate Control



Non-Chromate Control



Deft MUV on CrCC



Deft MUV on CeCC



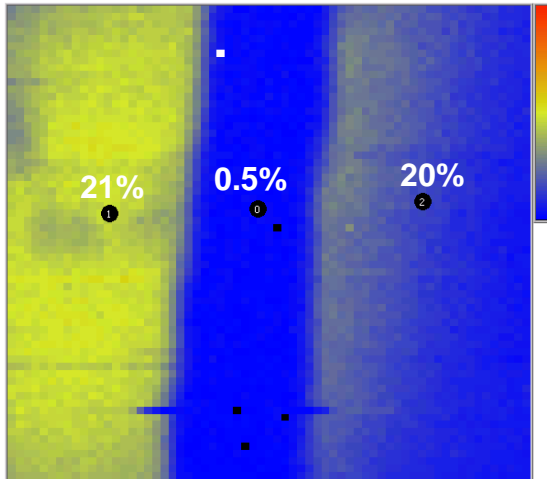
Hybricor 204 MUV on CrCC



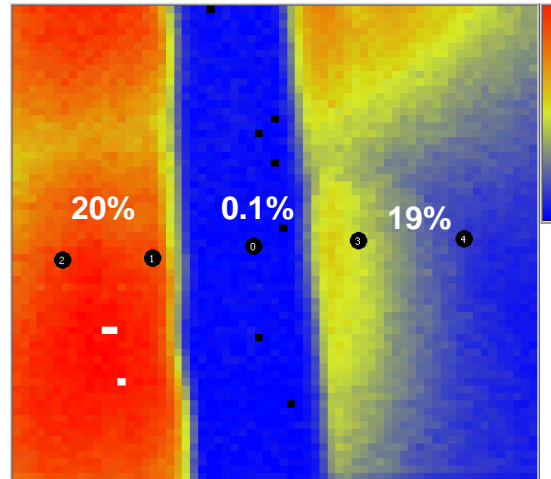
Hybricor 204 MUV on CeCC

Figure 36. Optical images of Stage 1 Al 2024-T3 coated panels after 3000 hours of neutral salt spray testing and removal of the corrosion coatings.

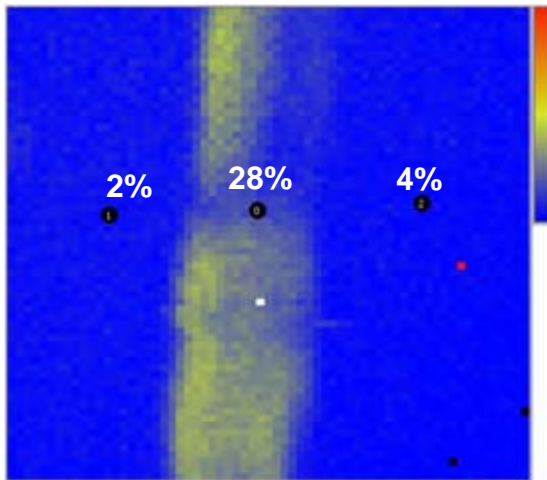
Characterization of the MUV stripped Hybricor 204 panels using mapping Auger spectroscopy was done to determine what, if any, differences between the panels could be detected. Panels which were coated, scribed, and then stripped, but not subjected to salt spray testing, were used as control panels for comparison of “before” and “after” salt spray testing. Shown in Figure 37 is Auger maps with the percentage of Al, Cr, and Zn measured near the scribe for Hybricor panels on a CrCC before and after salt spray testing. Zinc is one of the components of the Hybricor 204 compound. The scribe runs vertically down the middle in all cases; it is clearly demarked for the Cr and Ce signal maps with no salt spray exposure as the blue strip. The data indicate that corrosion protection of the Al substrate and scribe is related to the corrosion inhibitor from the MUV, in this case indicated by the presence of Zn on the panel. There was no Cr found in the scribe and Zn was not found in the scribe or on the surface before testing. After 3000 hours of salt spray testing, Zn was detected in the scribe and on the surface of the Al substrate, a strong indication that the corrosion inhibitor in MUV migrated and protected the panel. Similar results were found for Hybricor 204 panels that passed 3000 hours of ASTM B117 testing on CeCC (Figure 38), additional support that the MUV was actively protecting the Al against corrosion.



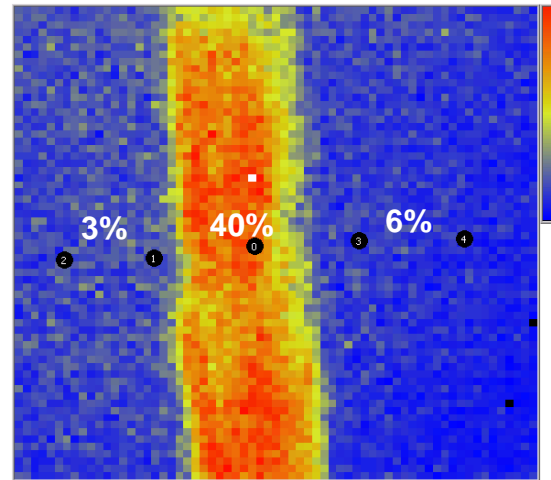
Cr Signal: No salt spray



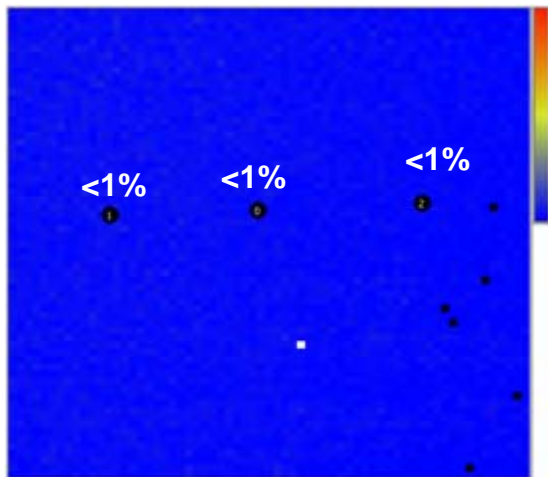
Cr Signal: After Passing 3000 hours



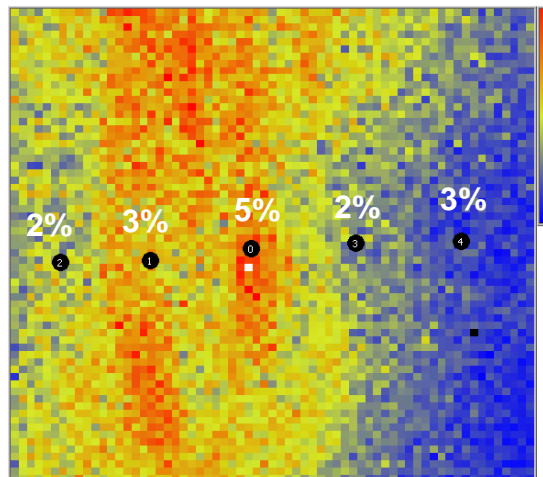
Al Signal: No salt spray



Al Signal: After Passing 3000 hours

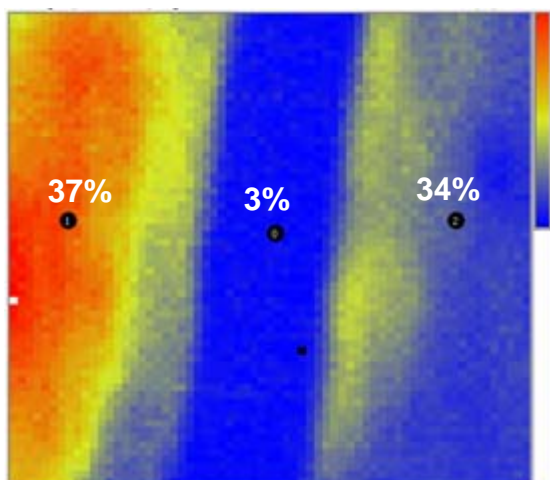


Zn Signal: No salt spray

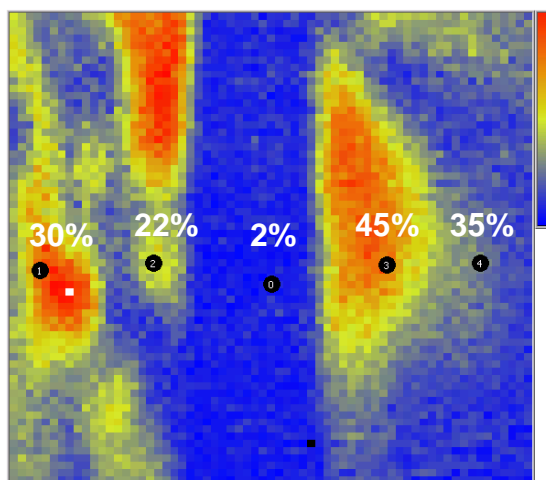


Zn Signal: After Passing 3000 hours

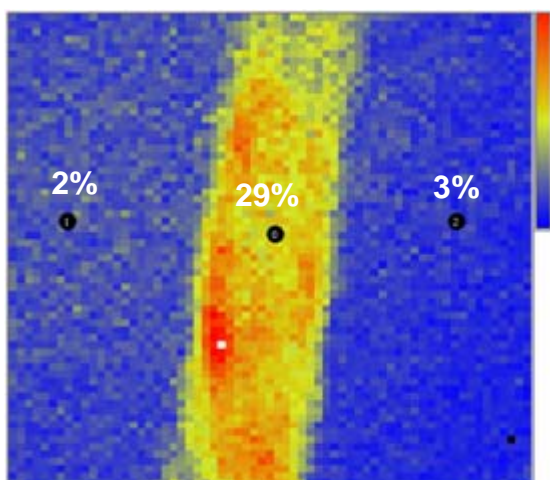
Figure 37. Auger maps for Cr, Al, and Zn near the scribe for two different Hybricor 204 MUV coated panels; one not exposed to salt spray and the other after passing 3000 hours salt spray.



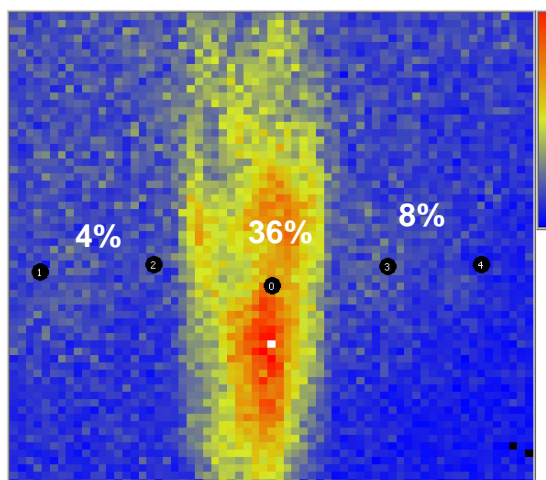
Ce Signal: No salt spray



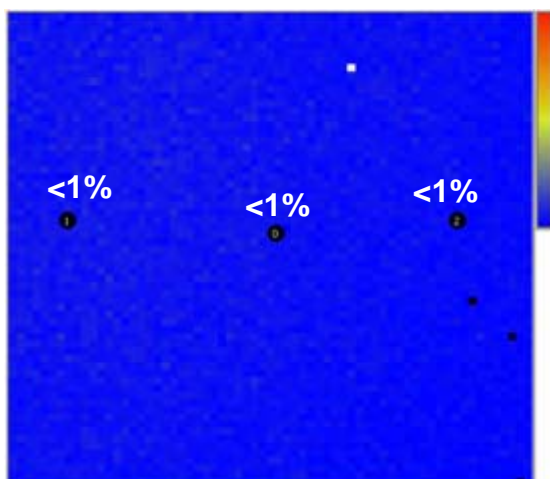
Ce Signal: After Passing 3000 hours



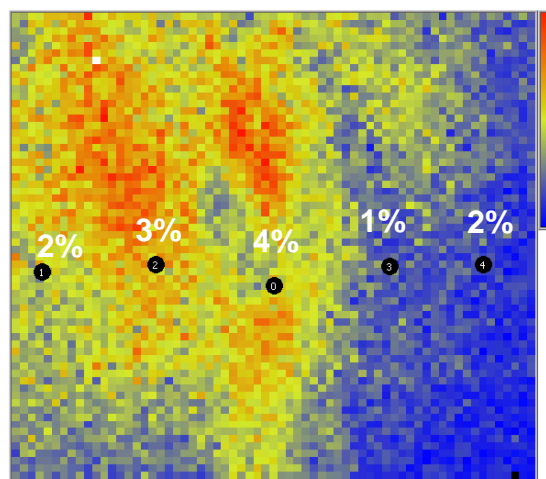
Al Signal: No salt spray



Al Signal: After Passing 3000 hours



Zn Signal: No salt spray



Zn Signal: After Passing 3000 hours

Figure 38. Auger maps for Ce, Al, and Zn near the scribe for two different Hybricor 204 MUV coated panels; one not exposed to salt spray and the other after passing 3000 hours salt spray.

Round 2 MUV Evaluations

Based on the promising results of Round 1 testing, a more complete set of tests was conducted on MUV coatings during Round 2, including filiform, adhesion, fuel resistance, SO₂ spray, and Xe arc weathering in addition to the neutral salt spray testing. Multifunctional UV coatings were applied to CrCC, CeCC, tri-valent chromium (TCP), and bare Al 2024-T3 panels, and chromate and non-chromate panels were again used as controls. Hybricor 204, Deft, HT-13, and HT-20 corrosion inhibitors, as well as different monomers, were evaluated. The experimental matrix was exploratory in nature such that the test results were expected to vary widely. This approach was taken to help identify and optimize the key performance variables in the MUV coating system. In general, the MUV coatings with Hybricor 204 corrosion inhibitor and IBOA monomer on CrCC performed better than other MUV inhibitor, monomer, and conversion coating systems, but not as well as the chromate controls. In most cases the MUV coating systems with Hybricor 204 inhibitor on CrCC were close to passing all of the performance requirements. The results were considered encouraging but not definitive. Shown in Figure 39 are the chromate and non-chromate Al 2024-T3 control panels after salt spray testing along with Hybricor 204 loaded MUV coatings on CrCC and CeCC Al 2024-T3 panels.

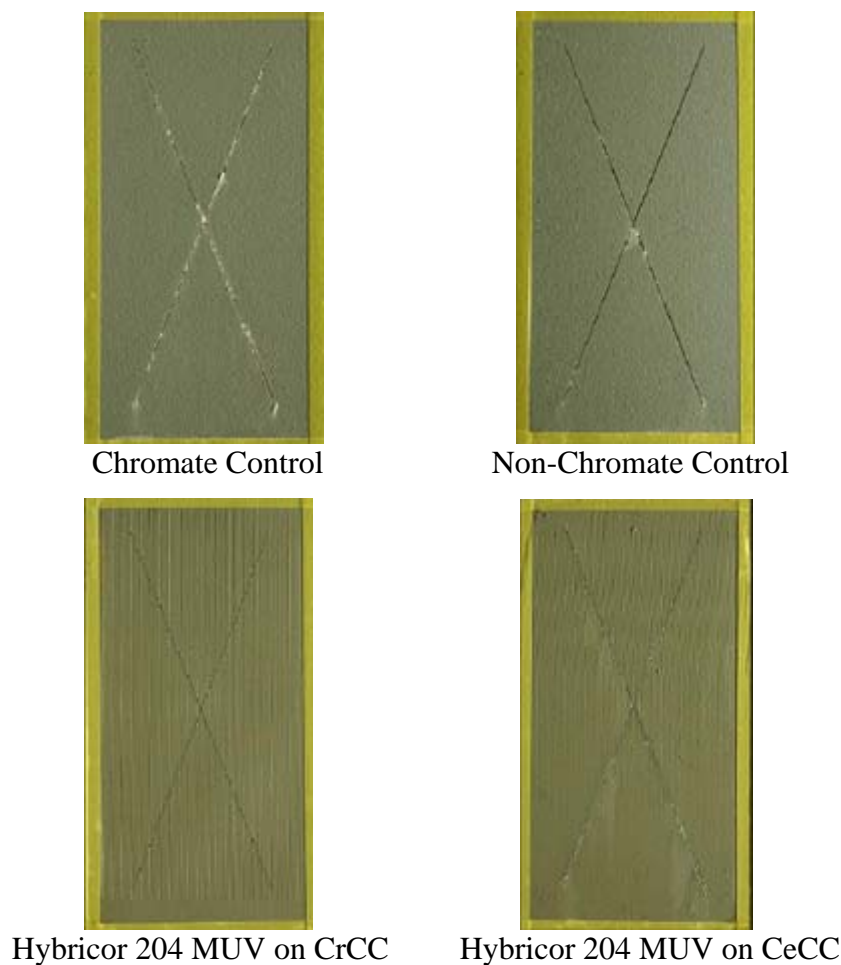


Figure 39. Optical images of Round 2 Al 2024-T3 coated panels after 2000 hours of neutral salt spray testing.

In response to a SERDP action item, results from salt spray testing of MUV coatings with Hybricor 204 on TCP and bare Al 2024-T3 are presented in Figures 40 and 41. The TCP conversion coatings with a Hybricor 204 loaded MUV (Figure 40) looked similar to the CeCC results with a little salting in the scribes but the MUV in direct contact with the Al substrate had numerous blisters and significant salting in the scribe (Figure 41).



Figure 40. Optical image of a Round 2 Hybricor 204 MUV coated Al 2024-T3 panel with a TCP conversion coating after 2000 hours salt spray.



Figure 41. Optical image of a Round 2 Hybricor 204 MUV coated Al 2024-T3 panel that did not have a conversion coating (bare) after 2000 hours salt spray.

Filiform corrosion testing was conducted on Alclad 2024-T3 substrates (i.e. Al roll bonded to Al 2024-T3) out to 1000 hours of testing. Figure 42 depicts the control, HT-13 MUV, and Hybricor 204 MUV panels after filiform testing. Chrome and chrome-free controls passed filiform testing as did the Hybricor 204 on CrCC as all corrosion was less than 1/4" from the scribe and most were less than 1/8" away from the scribe. The corrosion away from the scribe for the HT-13 MUV panels after filiform testing was just outside the test specifications, as was also the case for the CeCC panels with MUV coatings. These results were considered promising for a first attempt.

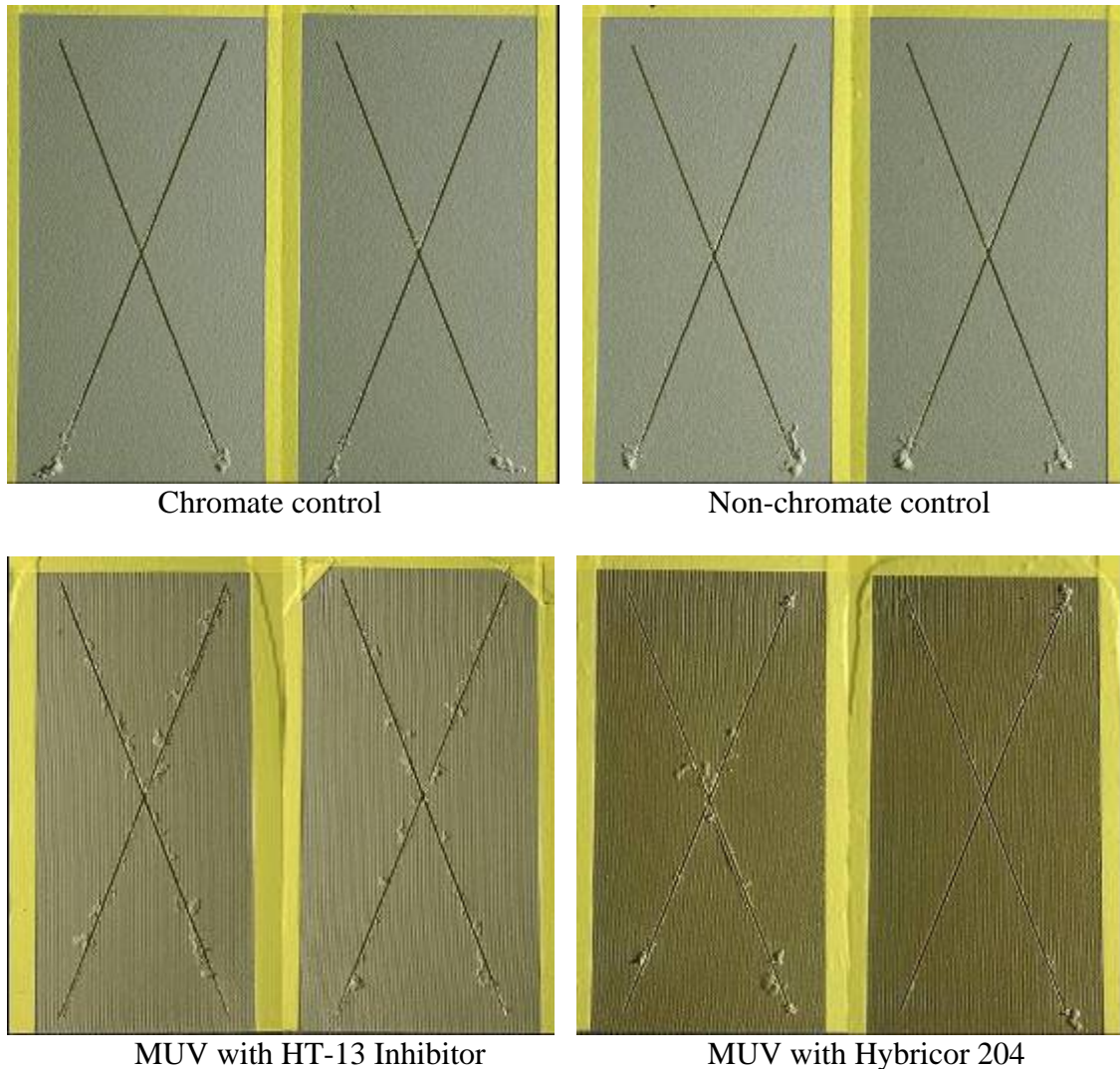


Figure 42. Images of integrated coatings on CrCC Al clad Al 2024-T3 after 1000 hours of filiform corrosion testing.

Ladder Studies between Round 2 and Round 3

Multifunctional UV curable coatings applied by drawbar (draw-downs) resulted in Hybricor 204 corrosion inhibitor from Wayne Pigments demonstrating the best performance during salt spray testing of scribed Al 2024-T3 panels with chromate conversion coatings (CrCC). The initial work used a ~36 wt% charge level of the Hybricor 204, and ladder studies indicated that charge levels near 30% were also effective at prevent salting of scribe lines during salt spray testing. Additional ladder studies were then conducted at charge levels of 36.4%, 34.6%, 32.8%, 30.9%, 29.1%, and 27.3% to determine the optimum value, as lowering the charge level improves other properties such as flexibility. All of the MUV coatings in the study were applied to CrCC Al 2024 substrates using a drawbar. Other than samples that had adhesion failures related to substrate preparation, each of the charge levels had a panel with 1,A ratings after 3000 hours of ASTM B117 testing. Images of the panels after 3000 hours of salt spray testing are shown in Figure 43. Taking into account a number of factors, the 29.1% charge level was chosen for subsequent work to develop a MUV spray deposition process.

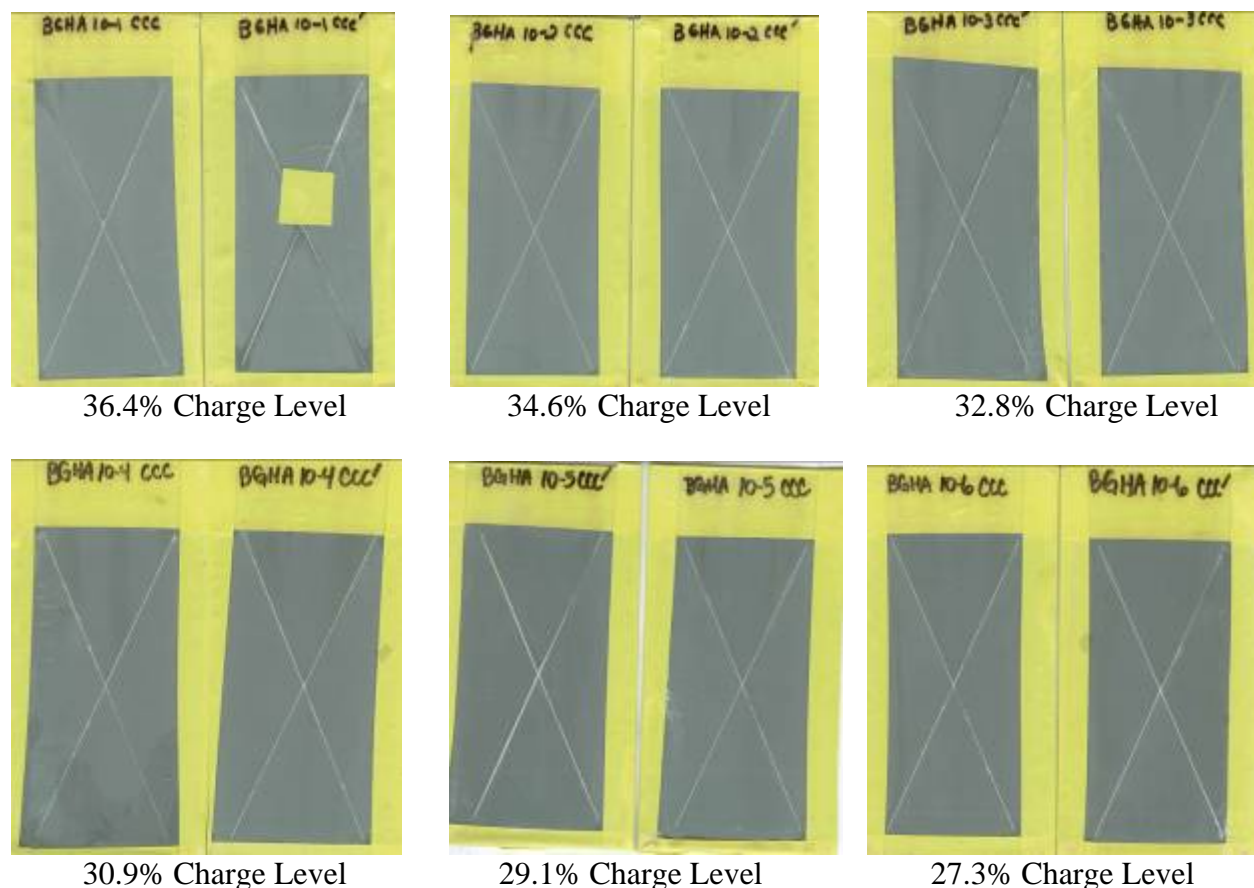


Figure 43. Optical images of MUV coated Al 2024-T3 panels with different charge levels of Hybricor 204 corrosion inhibitor after 3000 hours of salt spray testing.

Round 3 MUV Evaluations

After determining the amount of Hybricor 204 corrosion inhibitor to use in the MUV, efforts were then focused on developing a MUV formulation that could be spray applied. It was found that the gloss values for sprayed panels were higher than those for corresponding draw-downs, so formulation adjustments were made to lower gloss and to improve sprayability, flow, and appearance. A study of additional dispersing aids for the Hybricor 204 corrosion inhibitor indicated that lower viscosity and better coating sprayability could be obtained with Solsperse hyperdispersants. The best results were obtained with Solsperse 39000, which was incorporated into the formulation. Adjustments were also made to the photoinitiator blend, monomer blend, oligomer, and level of filler used. A different black pigment was incorporated along with an improved package for stable weatherability and an additive for improved flow. The modified MUV coating on CrCC aluminum panels exhibited 5B adhesion (100%), reverse impact strength flexibility of 14 inch-lbs, resistance to >200 MEK double rubs, and good appearance with 20° gloss = 0.5, 60° gloss = 4.3, and 85° gloss = 7.6.

After adjustments to the MUV formulation had been made, coatings were applied to Al 2024-T3 and Al 7075-T6 substrates with CrCC, CeCC, and TCP using the modified low gloss gray MUV coating sprayed onto the panels. Chromate and non-chromate coated control panels using commercially available materials were also prepared. A listing of the panels tested and coatings used in the study are presented in Table IV.

Table IV - Coating Systems Evaluated (Round 3)

<i>Panel ID</i>	<i>Pretreatment</i>	<i>Coating system</i>
A	Chromate conversion coating, MIL-C-5541/PS13209 and Thin film sulfuric acid anodized per PS 13201 TY II with 2 minute dichromate seal (flexibility panels only)	MUV (Hybricor 204)
B	CeCC	MUV (Hybricor 204)
C	TCP	Deft 65GN015 primer, PPG CA8211/F36375/CA8200B top coat(chrome free control)
D	Chromate conversion coating, MIL-C-5541/PS13209 and Thin film sulfuric acid anodized per PS 13201 TY II with 2 minute dichromate seal (flexibility panels only)	Deft 44GN072 primer, PPG CA8211/F36375/CA8200B (chromated control)

Chromate conversion coated panels had good appearance but the appearance of the coating on cerium conversion coated panels was not as good, with some wrinkling at higher coating thicknesses (Figure 44). Appearance was better on Alclad panels which had a lighter cerium conversion coat.

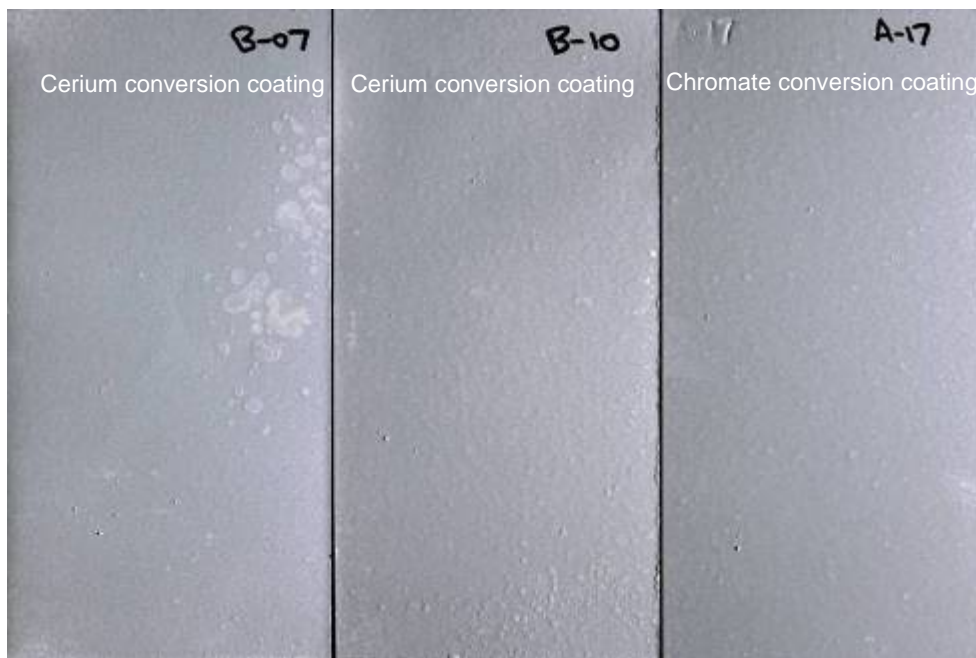


Figure 44. Optical images of MUV coated Al 2024-T3 panels on CeCC and CrCC pretreatments.

After the panels were prepared, evaluation was conducted at Boeing. The wet tape adhesion tests indicated that the MUV and chromate primer on CrCC passed with images of the panels shown in Figure 45. Exposure of the panels to Skydrol fluid for thirty days and measurement of the pencil hardness resulted in only the chromate control panels passing the test. All of the other coating combinations failed, with complete loss of adhesion occurring for MUV spray coatings on CeCC. Exposure of panels to xenon-arc radiation for 1000 hours as an accelerated weathering test was also conducted. Measurement of the changes in optical appearance and color were recorded at the 500 and 1000 hour mark. The results indicated that the chromate and non-chromate control panels passed the test, with a spectral loss of less than 5 at 60° and a delta E of less than 1. The MUV coatings had gloss values of ~2, meeting the specification, but the delta E values were close to 5, well above the requirement.

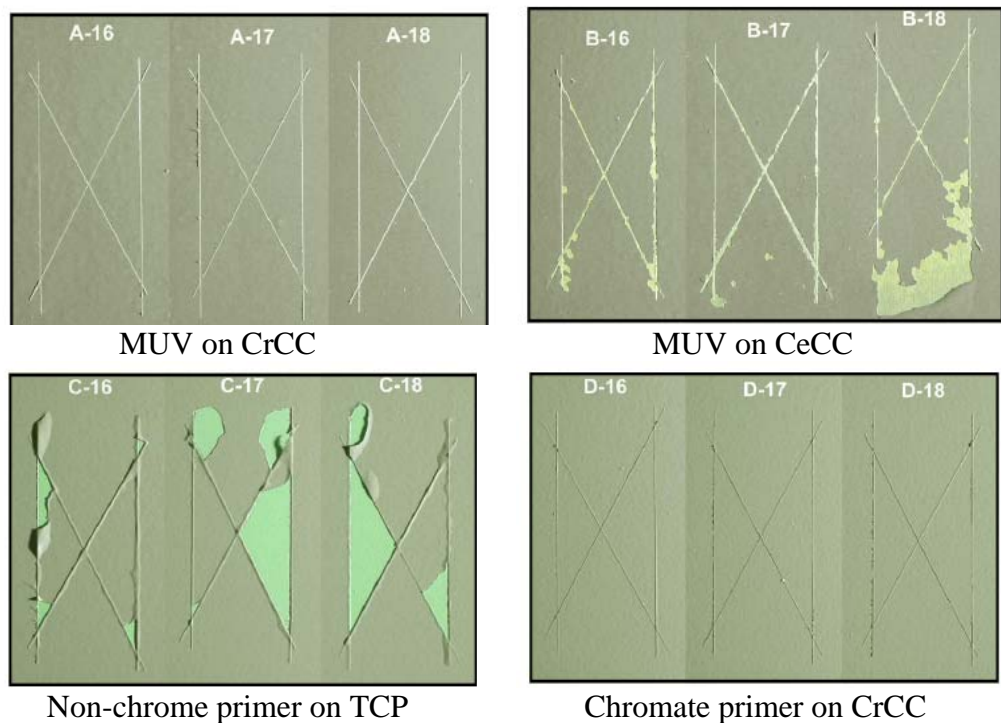
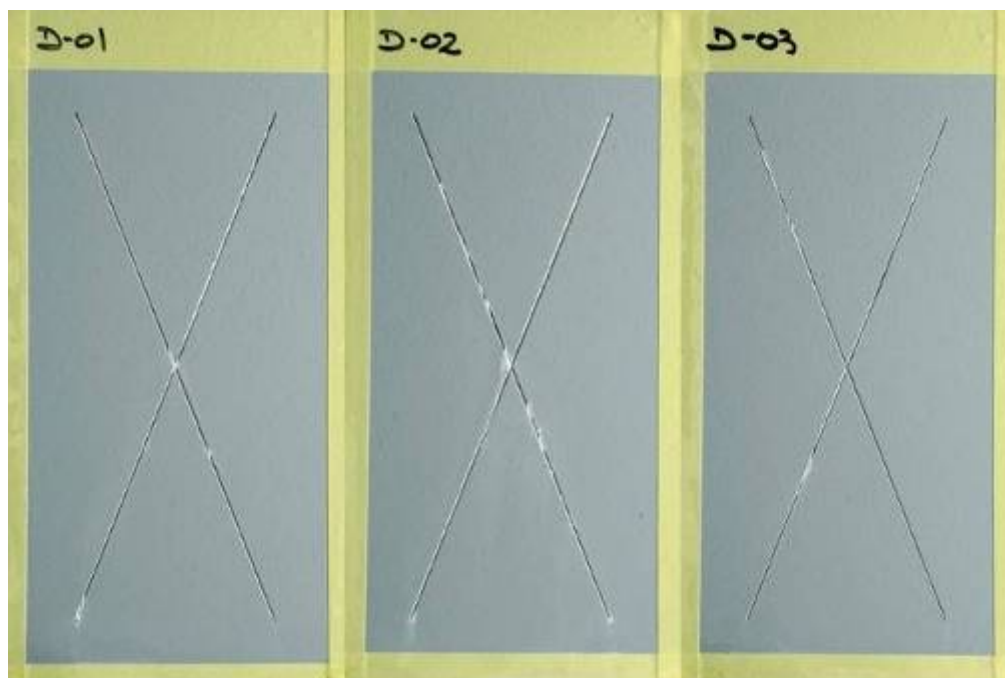


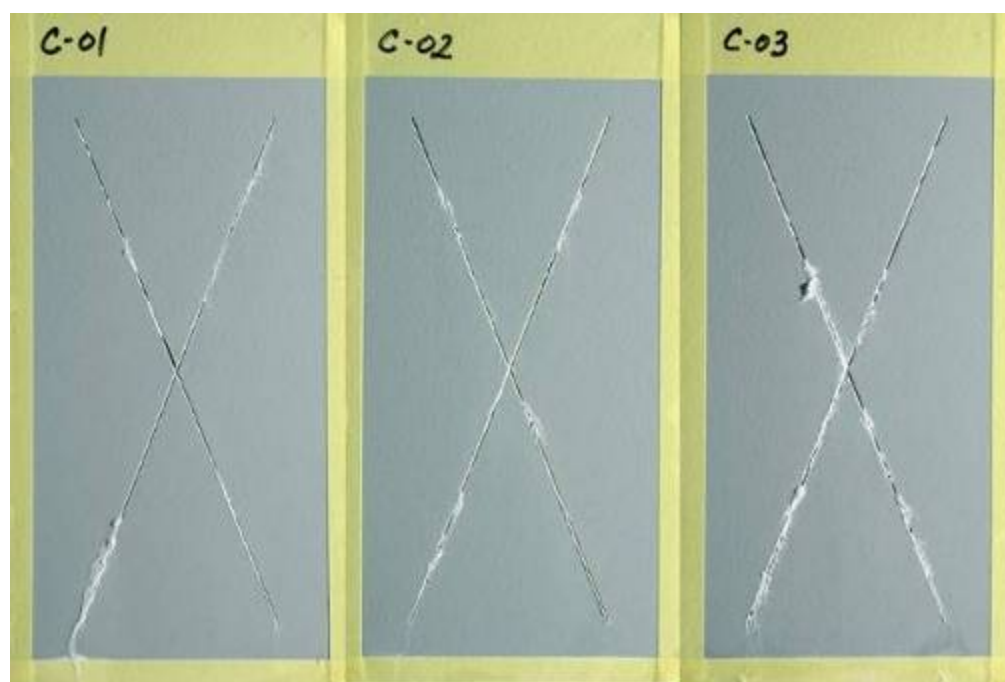
Figure 45. Optical images of wet scribe test results.

Filiform corrosion for 1000 hours on Alclad 2024-T3 and Alclad 7075-T6 substrates was performed. The chromate control panels for both 2024 and 7075 passed the test while the non-chromate controls passed on 2024 but failed on 7075, with the MUV coatings on CrCC and CeCC failing on both substrates.

Neutral salt spray testing of control and MUV coated CrCC, CeCC, and TCP pretreatments on Al 2024-T3 and Al 7075-T6 panels was done out to 3000 hours with ratings assessed every 1000 hours. The chromate and non-chromate controls performed the best, with 1,A or 2,A ratings, with the MUV on CrCC (2,4,A) ratings next best. The MUV coatings on TCP and CeCC had the lowest rankings (2,4,9,H typical). Pictures of the panels after 3000 hours of ASTM B117 testing are presented in Figures 46-48.

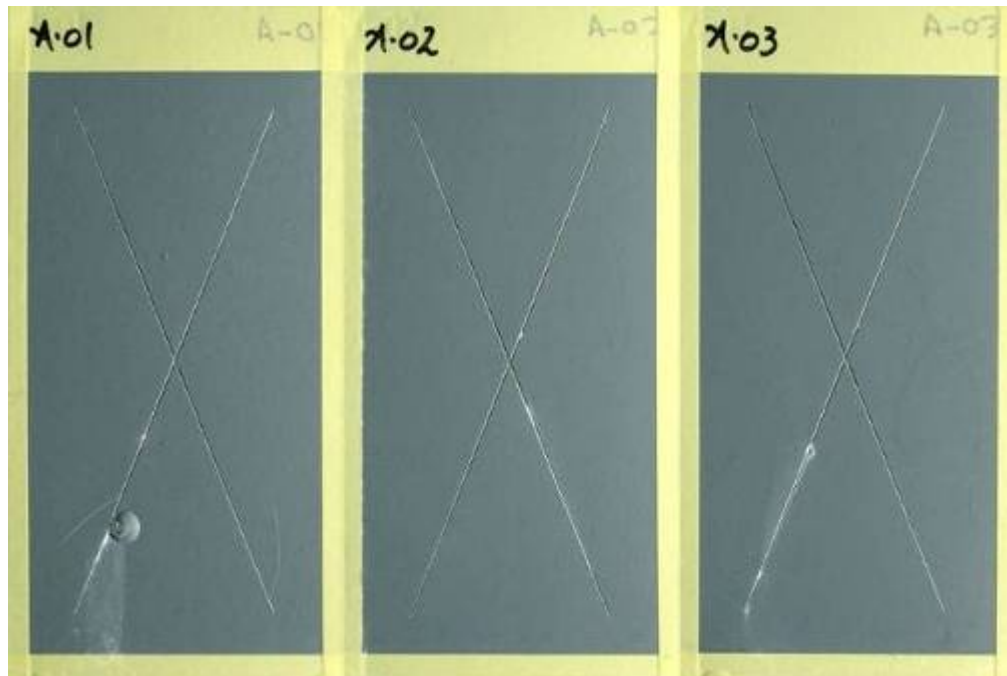


Chromate Primer on CrCC

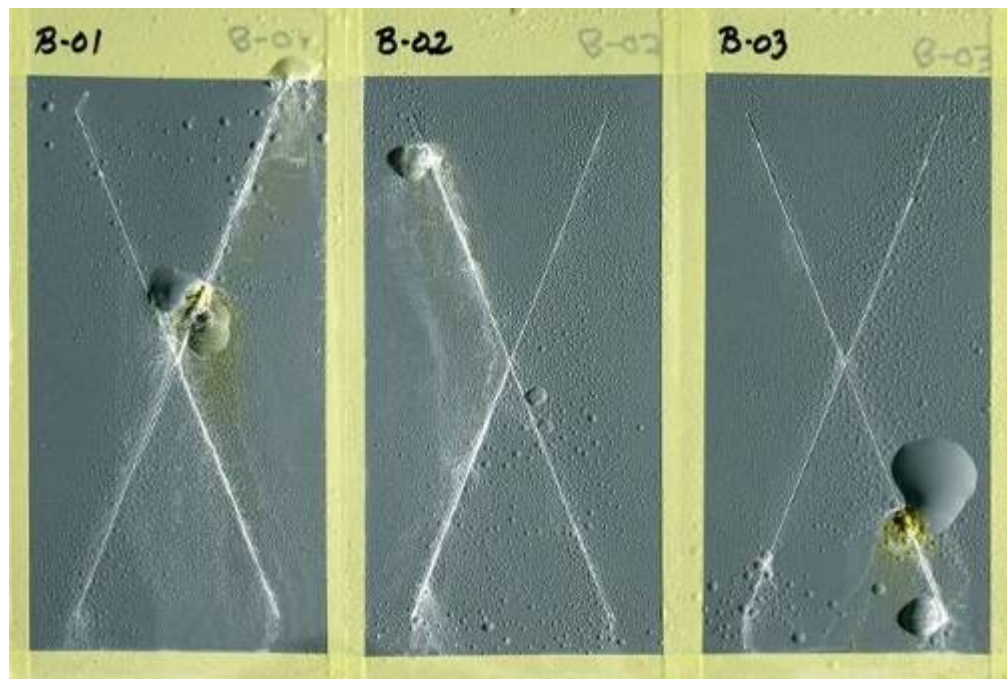


Non-chromate Primer on TCP

Figure 46. Optical images of Al 2024-T3 control panels after 3000 hours of salt spray corrosion testing.



MUV on CrCC



MUV on CeCC

Figure 47. Optical images of MUV coated Al 2024-T3 panels with CrCC and CeCC pretreatments after 3000 hours of salt spray corrosion testing.



MUV on TCP

Figure 48. Optical images of MUV coated Al 2024-T3 panels with TCP pretreatments after 3000 hours of salt spray corrosion testing.

Overall the performance of the coatings was not as good on Al 7075-T6 panels as the Al 2024-T3 panels, with no coating systems rated 1,A after 3000 hours. The chromate and non-chromate control ratings were ~2,4,A as were the MUV on CrCC panels. The MUV on CeCC had a rating of ~3,5,9,H. The MUV on CrCC was given the #1 rank after 3000 hours. Figures 49 and 50 are images of the panels after salt spray testing.

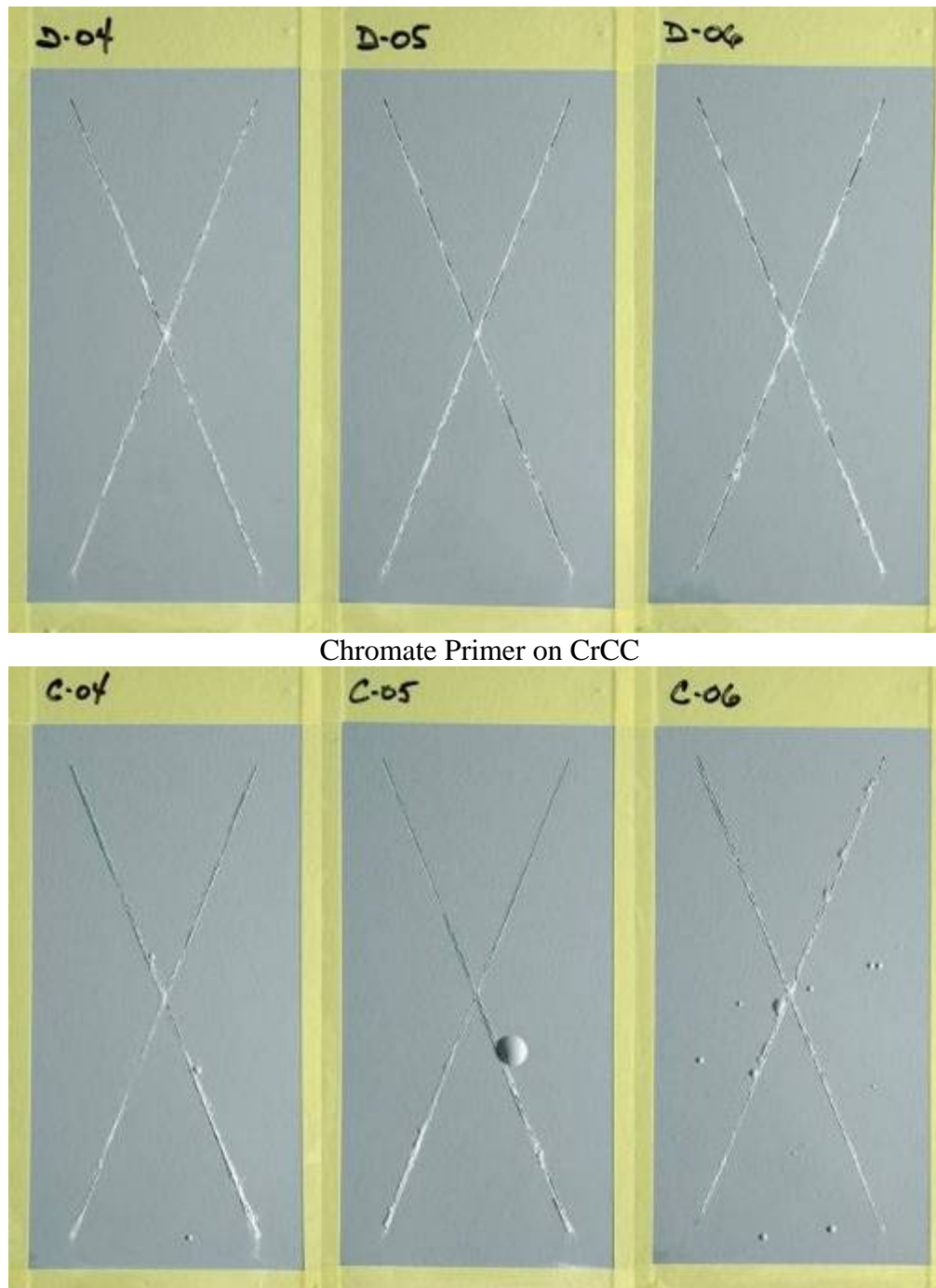
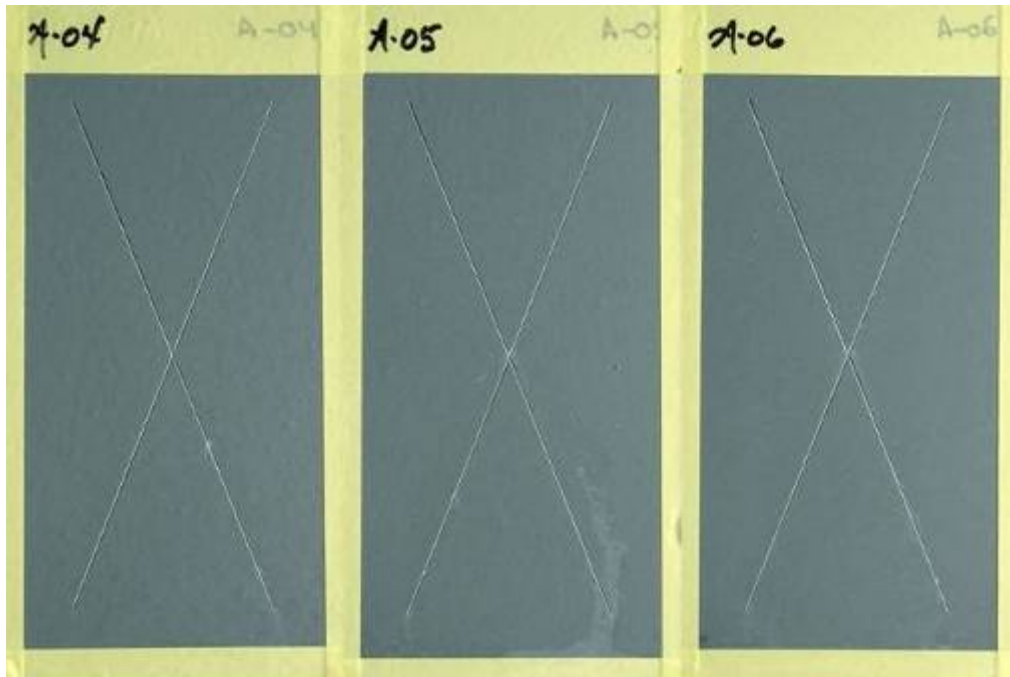
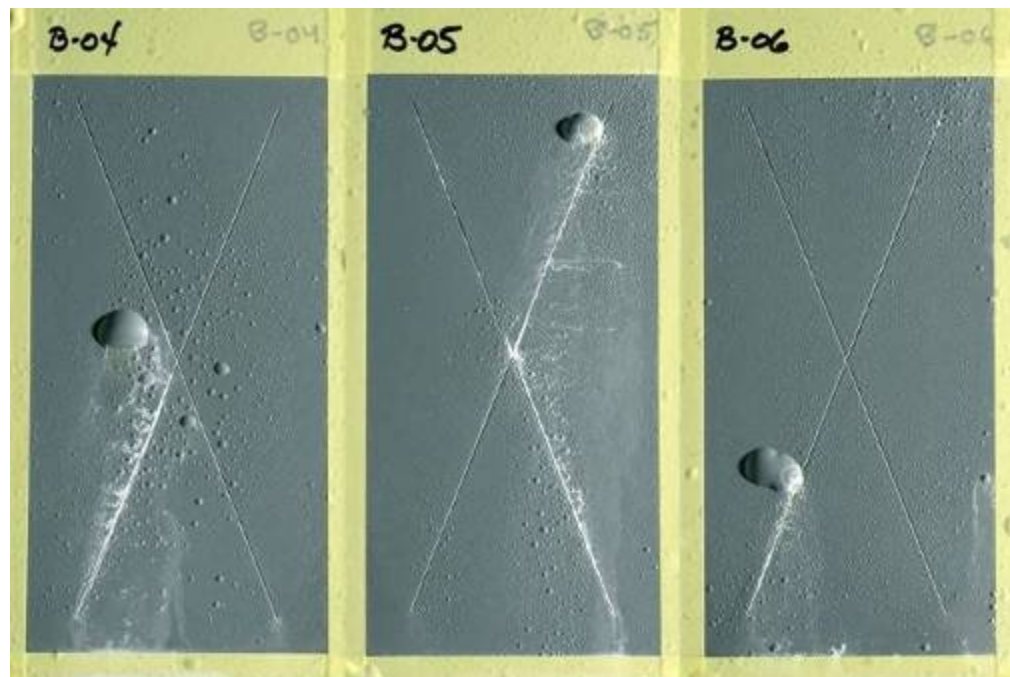


Figure 49. Optical images of Al 7075-T6 control panels after 3000 hours of salt spray corrosion testing.



MUV on CrCC



MUV on CeCC

Figure 50. Optical images of MUV coated Al 7075-T6 panels with CrCC and CeCC pretreatments after 3000 hours of salt spray corrosion testing.

MUV Coated CeCC Studies

The results from the Round 3 testing clearly indicated that improvement in the salt spray performance of the MUV on CeCC was needed. A test matrix of CeCCs deposited under different conditions that were then sprayed with the same formulation of MUV was carried out. Salt spray testing was done out to 2000 hours. The results were encouraging as a few panels had 1,A ratings while most of the panels had 1 ratings in combination with blisters (rating 8). The heat treated and fluoroboric acid cleaned Al 2024-T3 samples did well as did the fluoroboric acid cleaned Al 7075-T6 substrates. Blistering under the MUV coating was a common flaw for all conditions.

In October 2008 all of the team members met at the Light Curable Coatings (LCC) facility in Berea, OH to process and coat panels (Table V). This was done in order to investigate how depositing the CeCC and then MUV coating within minutes of each operation affected coating performance. In addition to the CeCC samples made at LCC, CeCC panels were also made in Rolla the day before the trip so that a comparison could be made. All samples were MUV coated and cured at LCC. The CeCCs made at LCC were blow dried with air for 5 minutes before the MUV coating was spray deposited. Among the CeCC variables investigated were the number of spray cycles, post treatment sealing temperature, and cleaning/surface preparation process. In some cases the MUV was sprayed directly onto the cleaned panel without a conversion coating.

Table V - Test Matrix for MUV/CeCC Panels Done at LCC Oct 2008

Condition	Alloy	Surface Prep.	Coating	Post Treatment	Notes	Panel Numbers
1	2024	standard	3 sprays	55 C		1-(1-3)
1R	2024	standard	3 sprays	55 C	sprayed at MST	1R-(1-6)
2	2024	standard	3 sprays	85 C		2-(1-6)
2R	2024	standard	3 sprays	85 C		2R-(1-6)
2A	2024	standard	3 sprays	85 C	pH	2A-(1-3)
2B	2024	standard	3 sprays	85 C	dry overnight	2B-(1-6)
3	2024	standard	1 spray	85 C		3-(1-6)
3A	2024	standard	1 spray	85 C	pH	3A-(1-3)
3B	2024	standard	1 spray	85 C	dry overnight	3B-(1-6)
4	2024	standard	5 sprays	85 C		4-(1-6)
4A	2024	standard	5 sprays	85 C	pH	4A-(1-3)
4B	2024	standard	5 sprays	85 C	dry overnight	4B-(1-3)
5	2024	turco only	no Ce coating	N/A		5-(1-6)
5R	2024	turco only	no Ce coating	N/A	sprayed at MST	5R-(1-6)
6	2024	turco and acid	no Ce coating	N/A		6-(1-6)
6R	2024	turco and acid	no Ce coating	N/A	sprayed at MST	6R-(1-6)
7	2024	standard	brush (1 stroke)	85 C		7-(1-6)
7R	2024	standard	brush (1 stroke)	85 C	brushed at MST	7R-(1-6)
8	2024	standard	wipe (1 stroke)	85 C		8-(1-6)
8R	2024	standard	wipe (1 stroke)	85 C	brushed at MST	8R-(1-6)
9	2024	standard	5 sprays	85 C	UV treatment before MUV application	9-(1-6)
9A	2024	standard	5 sprays	not sealed	UV treatment before MUV application	9A-(1-6)
10	2024	Cu seeding	3 sprays	85 C		10-(1-6)
10R	2024	Cu seeding	3 sprays	85 C	sprayed at MST	10R-(1-6)
11	7075	Cu seeding	3 sprays	85 C		11-(1-6)
11R	7075	Cu seeding	3 sprays	85 C	sprayed at MST	11R-(1-6)
12	2024	Luna	no Ce coating	85 C		12-(1-5)
12R	2024	Luna	no Ce coating	85 C	prepared at MST 1x3	12R-(1-6)
13	7075	standard	3 sprays	85 C		13-(1-6)
13 R	7075	standard	3 sprays	85 C	sprayed at MST	13R-(1-6)

Presented in Table VI are some of the results from evaluation of the MUV/CeCC panels done at LCC. Most of the test conditions on Al 2024-T3 substrates resulted in adequate pencil hardness values (>H), reasonable adhesion ratings (>4B), 60° gloss values <5, greater than 200 MEK rubs without coating removal, and maintaining integrity after 24 hour Skydrol fluid exposure. The panels that did not do as well were related to using a lower temperature (55°C) post treatment step, a thicker CeCC layer (5 spray cycles), and brush or wipe application of the CeCC. Data from MUV on bare Al 2024-T3 substrates (no conversion coating) were comparable to the results from the panels with a CeCC. The results on Al 7075-T6 panels (condition 13) were poor in almost all cases.

**Table VI - Pencil Hardness, Adhesion, Gloss, MEK Rub and Skydrol Results
for MUV/CeCC Panels Done at LCC Oct 2008**

<u>CONDITION/PANEL</u>	<u>PENCIL</u>		<u>GLOSS</u>			<u>24 HR</u>	
	<u>HARDNESS</u>	<u>ADHESION</u>	<u>20°</u> <u>60°</u>		<u>85°</u>	<u>MEK RUBS</u>	<u>SKYDROL</u>
CONDITION 1-3	F	0B	0.6	5.0	9.6	60 RUBS	FAILED
CONDITION 1R-5	4H	3B	0.5	3.6	7.9	>200 RUBS	PASSED
CONDITION 2-6	4H	3B	0.5	3.8	7.8	>200 RUBS	PASSED
CONDITION 2R-1	3H	4B	0.7	5.4	11.3	>200 RUBS	PASSED
CONDITION 2A-1	2H	3B	0.5	3.7	7.9	>200 RUBS	PASSED
CONDITION 2B-4	F	3B	0.6	4.6	9.5	>200 RUBS	PASSED
CONDITION 3-1	4H	5B	0.6	5.1	12.7	>200 RUBS	PASSED
CONDITION 3A-3	4H	4B	0.5	3.8	8.7	>200 RUBS	PASSED
CONDITION 3B-2	4H	4B	0.5	4.5	8.8	>200 RUBS	PASSED
CONDITION 4-3	F	1B	0.5	3.6	8.9	>200 RUBS	PASSED
CONDITION 4A-3	H	2B	0.5	3.6	7.6	>200 RUBS	PASSED
CONDITION 4B-3	2H	2B	0.5	4.5	9.7	>200 RUBS	PASSED
CONDITION 5-1	3H	3B	0.6	4.6	9.4	>200 RUBS	PASSED
CONDITION 5R-1	4H	4B	0.5	4.3	8.0	>200 RUBS	PASSED
CONDITION 6-1	4H	5B	0.5	4.1	8.2	>200 RUBS	PASSED
CONDITION 6R-1	4H	5B	0.5	4.4	9.5	>200 RUBS	PASSED
CONDITION 7-1	4H	2B	0.5	4.4	11.3	195 RUBS	PASSED
CONDITION 7R-1	4H	5B	0.5	4.1	9.2	>200 RUBS	PASSED
CONDITION 8-1	4H	2B	0.5	4.4	8.4	>200 RUBS	PASSED
CONDITION 8R-1	3H	1B	0.7	5.6	11.6	190 RUBS	PASSED
CONDITION 9-3	4H	5B	0.6	4.4	8.2	>200 RUBS	PASSED
CONDITION 9A-2	2H	4B	0.4	3.6	9.3	>200 RUBS	PASSED
CONDITION 10-1	4H	5B	0.6	4.5	8.2	>200 RUBS	PASSED
CONDITION 10R-1	4H	5B	0.6	5.2	10.8	>200 RUBS	PASSED
CONDITION 11-3	4H	3B	0.6	4.6	11.3	>200 RUBS	PASSED
CONDITION 11R	4H	5B	0.6	5.0	10.3	>200 RUBS	PASSED
CONDITION 12-3	4H	4B	0.4	3.3	7.6	>200 RUBS	PASSED
CONDITION 12R-1	F	4B	0.6	4.8	10.1	145 RUBS	FAILED
CONDITION 13-4	2H	0B	0.6	4.6	11.8	175 RUBS	FAILED
CONDITION 13R-5	2H	0B	0.8	6.3	12.7	98 RUBS	FAILED

Pencil Hardness Scale: 9B<8B<7B<6B<5B<4B<3B<2B<B<HB<F<H<2H<3H<4H<5H<6H<7H<8H<9H

Cross-hatch adhesion percentages: 0B (0% to 35%), 1B (35% to 65%), 2B (65% to 85%), 3B (85% to 95%), 4B (over 95%), 5B (100%)

Salt spray testing of the MUV/CeCC panels made at LCC was done along with control panels of MUV on CrCC (labeled QCCC) and MUV directly on bare Al-2024 T3 substrates. The ratings for the panels after 500 and 1000 hours are listed in Table VII. Although the scribe lines were still shiny for many of the test panels after 1000 hours of salt spray testing, most of the cerium conversion coated panels contained blisters, and the only conditions that had any 1A ratings after 1000 hours of testing were conditions with no CeCC and one that had UV treatment prior to MUV deposition, and the control MUV on QCCC panels.

Table VII - Salt Spray Ratings for MUV/CeCC Panels Done at LCC Oct 2008

Effect Of CeCC Variables On Corrosion Resistance Of Sprayed MUV Films For MS&T 10/2008 Test Matrix

CONDITION/PANEL	Initial Film Build (mils)				Corrosion Inspection & Scribe Line Ratings	
	Left	Top	Right	Bottom	500 Hrs	1000 Hrs
CONDITION 1-1	1.90	2.00	1.90	2.00	1,14,B	3,6,8,14,H
CONDITION 1-2	2.10	1.70	2.00	2.20	1,4,8,14,G	3,6,8,14,H
CONDITION 1R-1	1.15	1.50	1.45	1.50	1,A	1,4,8,E
CONDITION 1R-2	2.20	2.00	2.30	2.20	1,1,8,B	1,4,8,E
CONDITION 2-4	2.60	2.20	2.10	3.00	1,8,13,B	1,8,13,H
CONDITION 2-5	2.60	2.40	2.20	2.60	1,8,13,B	1,8,13,E
CONDITION 2R-5	1.70	2.10	1.15	2.20	1,8,B	1,8,G
CONDITION 2R-6	1.80	2.30	2.00	1.90	1,A	1,8,B
CONDITION 2A-2	2.10	2.20	2.10	1.80	1,8,13,B	1,8,13,D
CONDITION 2A-3	2.30	2.60	1.90	1.95	1,8,14,B	1,4,8,14,H
CONDITION 2B-1	2.40	1.55	2.40	1.85	1,4,8,13,B	1,4,8,13,H
CONDITION 2B-3	1.95	2.00	2.40	1.85	1,8,13,B	1,8,13,G
CONDITION 3-2	1.70	1.65	1.95	1.70	1,8,B	1,8,F
CONDITION 3-3	1.75	2.10	2.10	2.30	1,8,B	1,8,E
CONDITION 3A-1	2.10	1.70	1.40	2.00	1,8,B	2,5,8,B
CONDITION 3A-2	1.60	1.70	1.75	1.70	1,4,8,C	2,4,8,H
CONDITION 3B-1	2.60	2.50	2.15	2.20	1,4,8,C	1,4,8,13,D
CONDITION 3B-3	1.70	1.85	2.30	1.90	1,8,B	1,4,8,G
CONDITION 4-1	1.75	2.20	1.95	2.30	1,A	2,4,8,D
CONDITION 4-4	1.75	1.75	1.65	1.75	1,13,B	1,13,B
CONDITION 4A-1	1.50	1.80	1.35	1.45	2,4,8,14,B	3,6,8,14,E
CONDITION 4A-2	1.45	1.80	1.60	1.35	2,4,8,13,B	2,4,8,14,B
CONDITION 4B-1	2.40	2.60	2.50	3.00	1,4,8,14,C	1,4,8,14,H
CONDITION 4B-2	2.20	2.20	1.75	1.95	1,4,8,14,B	2,4,8,14,G
CONDITION 5-3	2.60	2.50	2.10	2.60	1,8,B	1,8,G
CONDITION 5-4	2.30	2.10	2.40	2.80	1,4,8,10,B	1,4,8,10,E
CONDITION 5R-5	1.80	2.40	1.75	1.60	1,8,B	1,8,C
CONDITION 5R-6	1.80	2.10	1.55	1.65	1,8,B	1,8,10,C
CONDITION 6-3	1.80	2.20	2.10	1.85	1,A	1,A
CONDITION 6-4	2.40	2.90	3.00	2.50	1,A	1,8,B
CONDITION 6R-2	1.85	2.10	2.20	2.20	1,A	1,A
CONDITION 6R-4	2.20	2.30	2.10	2.40	1,8,B	1,8,C
CONDITION 7-3	1.60	1.60	1.90	1.70	1,8,B	2,4,8,G
CONDITION 7-4	1.50	1.70	2.10	2.20	1,8,B	2,4,8,H
CONDITION 7R-3	1.65	1.55	1.60	1.75	1,8,C	1,8,C
CONDITION 7R-4	1.80	2.00	2.10	1.85	1,8,C	1,8,G
CONDITION 8-3	1.85	1.90	2.50	2.30	1,8,B	1,8,G
CONDITION 8-4	1.55	1.50	1.30	1.35	1,8,B	1,8,G
CONDITION 8R-2	1.90	1.70	1.80	1.60	1,4,8,D	1,4,8,F
CONDITION 8R-3	1.80	2.20	1.60	1.85	1,8,B	1,8,C
CONDITION 9-1	1.65	2.30	2.10	1.85	1,8,B	1,13,B
CONDITION 9-2	1.95	2.10	2.30	2.10	1,8,13,B	1,8,13,F
CONDITION 9A-1	1.75	1.70	1.45	1.20	1,A	1,A
CONDITION 9A-3	2.30	2.30	2.10	2.20	1,8,13,C	1,8,13,F
CONDITION 10-3	2.10	1.75	2.20	1.95	1,8,B	1,8,C
CONDITION 10-4	2.30	2.10	2.20	3.00	1,13,B	1,8,14,H
CONDITION 10R-3	1.70	2.10	2.10	2.40	1,8,B	1,8,C
CONDITION 10R-4	1.65	1.85	1.55	1.30	1,8,B	1,8,C
CONDITION 11-1	2.60	2.80	2.20	2.50	1,4,8,G	2,4,8,H
CONDITION 11-2	2.60	2.90	2.60	3.00	1,4,8,H	2,4,8,10,13,H
CONDITION 11R-2	1.85	2.00	1.60	1.70	1,4,A	2,4,8,C
CONDITION 11R-3	2.30	1.55	1.60	1.65	1,4,A	2,4,8,B
CONDITION 12-4	1.75	1.40	1.40	2.20	1,4,8,C	2,4,8,G
CONDITION 12-5	1.45	1.95	1.65	2.20	1,4,8,10,C	1,4,8,10,F
CONDITION 13-5	2.10	1.70	1.60	1.55	2,4,8,13,C	2,4,8,14,D
CONDITION 13-6	1.80	1.90	1.50	2.00	2,4,8,13,C	2,4,8,14,C
CONDITION 13R-2	2.20	1.95	1.90	2.10	2,4,8,B	2,4,8,C
CONDITION 13R-3	2.40	2.30	1.85	2.40	2,4,8,C	2,4,8,D
CONTROL QCCC-1	1.95	2.00	1.65	2.20	1,A	1,A
CONTROL QCCC-2	1.85	2.20	1.90	2.10	1,A	1,A
CONTROL 2024 BARE-1	2.20	2.00	2.10	2.20	1,8,B	1,8,E
CONTROL 2024 BARE-2	1.75	2.20	1.75	1.90	1,8,B	1,8,E

Round 4 MUV Evaluations

For the panels made and evaluated during Round 4 the corrosion inhibitor level was the same as Round 3 with changes to the formulation made to adjust the mechanical and physical properties of the MUV coating. Results indicated that ASTM B117 neutral salt spray test ratings were similar for MUV coatings on CrCC, chromate controls, and non-chromate controls on Al 2024 and Al 7075 substrates (Figures 51 and 52). Ratings for MUV on TCP on 2024 were ~ 2,A while MUV on cerium conversion coatings (CeCC) were ~3,E with many blisters.

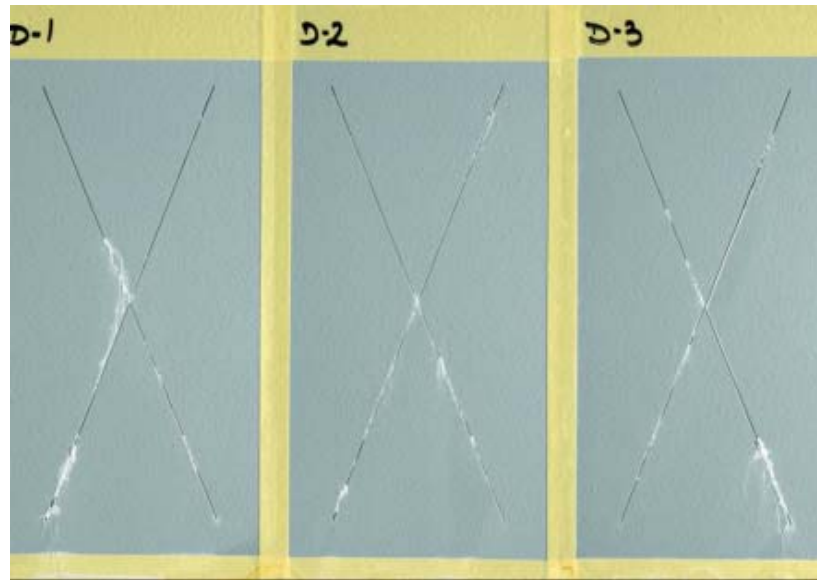


Figure 51. Al 2024-T3 chromate control panels after 3000 hours ASTM B117 testing.

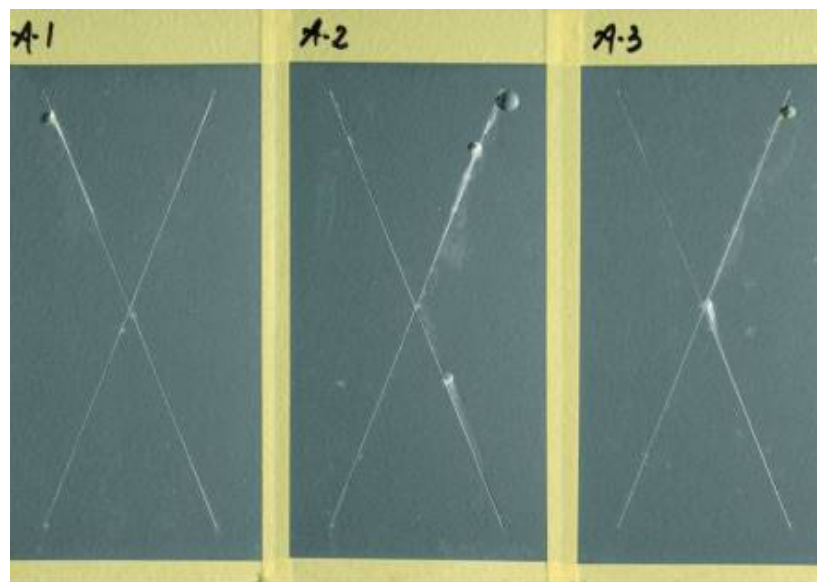


Figure 52. Al 2024-T3 panels with MUV on CrCC after 3000 hours ASTM B117 testing.

The MUVs were able to pass 200 MEK rub testing but coatings were unable to retain their integrity after a 24 hour Skydrol soak. The chromate and non-chromate controls passed wet tape adhesion and room temperature flexibility tests but the MUV coatings on CrCC and CeCC did not. Only the chromate controls passed low temperature flexibility tests. Xenon arc weathering of the chromate and non-chromate controls were within specifications but the change in the MUV coatings optical appearance were outside of the acceptable limits.

Chromate control and MUV coatings on CrCC passed filiform corrosion testing on Al 2024 and Al 7075 substrates. MUV coatings on CeCC passed on Al 7075 while non-chromate controls

passed on Al 2024. The corrosion performance of MUV coatings was excellent but adjustments to the MUV formulations did not improve the non-corrosion properties of the coatings.

Round 5 MUV Evaluations

Changes in MUV formulation were made to try to improve the physical properties of the MUV films from Round 4 while still maintaining corrosion inhibition. After 2000 hours of ASTM B117 neutral salt spray testing, the MUV coatings on chromate conversion coated (CrCC) Al 2024 and Al 7075 substrates had comparable ratings (1, 4, A) with the chromate controls in testing done at Boeing and Light Curable Coatings (Figure 53). Small blisters away from the scribe were present on the MUV coated panels. The non-chromate controls and MUV on TCP also had salting in the scribe after 2000 hours of ASTM B117 testing while the MUV panels on cerium conversion coated (CeCC) substrates had wide spread blister formation and salting in the scribe (Figure 54).

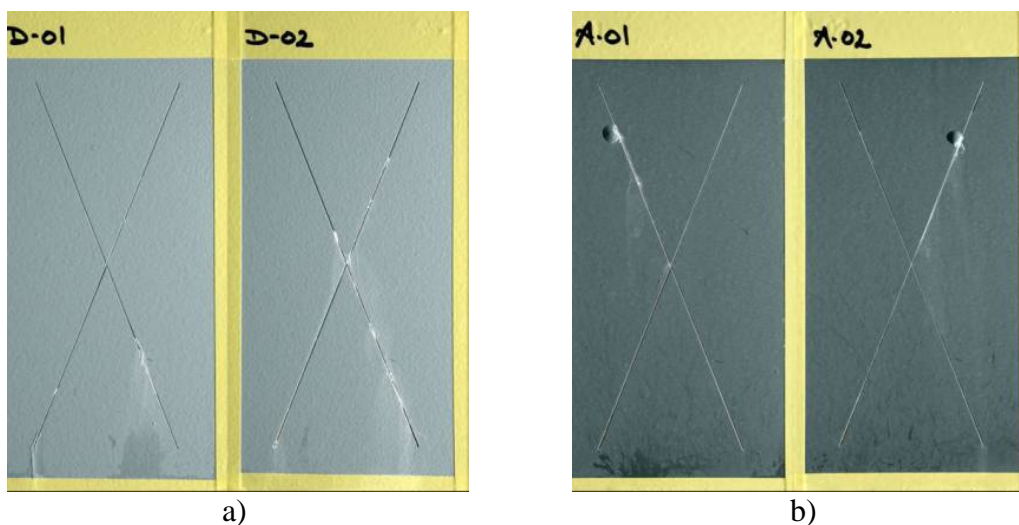


Figure 53. Optical images of Al 2024-T3 panels after 2000 hours of ASTM B117 salt spray testing: a) chromate standard and b) MUV on CrCC.

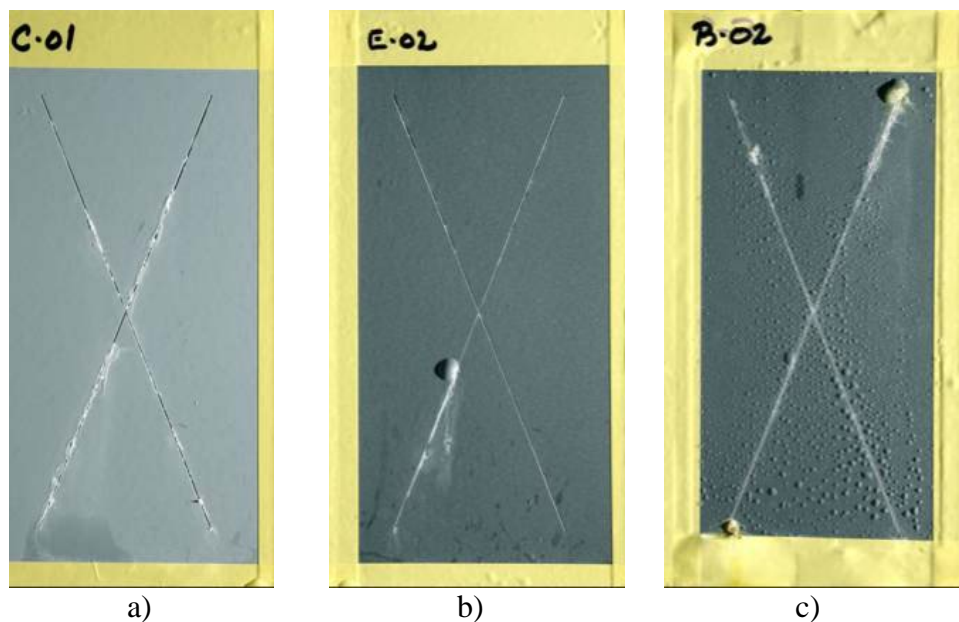


Figure 54. Optical images of Al 2024-T3 panels after 2000 hours of ASTM B117 salt spray testing: a) non-chromate standard, b) MUV on TCP, and c) MUV on CeCC.

MUV coatings with CrCC on Alclad 2024 and Alclad 7075 substrates passed filiform corrosion testing. MUV coatings with CeCC on Alclad 2024 passed filiform corrosion while MUV with CeCC on Alclad 7075 failed filiform testing. The chromate controls passed on Alclad 2024 and 7075 but the non-chromate controls failed on Alclad 2024 and 7075 substrates. Accelerated Xenon-arc weathering after 500 hours indicated that the 60 degree gloss reading was < 2 on the MUV coatings on CeCC and CrCC and 3 to 4 on the top coated chromate and non-chromate controls (maximum allowed value of 5). The delta E values for the controls was <1, within specifications, while the MUV coatings had a delta E of ~5 due to color darkening associated with the carbon pigment.

Initial pencil hardness of the control and MUV panels was 2H. The chromate and non-chromate control samples passed Skydrol resistance testing (3H after 30 days) while the MUV coatings on CrCC and CeCC failed (less than 6B after 30 days). All 3 of the chromate control and 2 of the 3 MUV/CrCC samples passed the low temperature flexibility tests (Figure 55). Room temperature flexibility test results indicated that the chromate and non-chromate controls had 20% elongation before cracking was observed at 10X magnification, 2 of the 3 MUV on CrCC had 10% elongation before cracking, and the MUV on CeCC had cracks visible at only a few % elongation (Figure 56). Investigations into the source and nature of the blisters that were observed after salt spray testing of MUV coatings on CeCC were conducted. Results indicate that blisters did not form after exposure to 40°C ambient or 85% relative humidity at 40°C for up to two weeks. Blisters only formed during submersion of the panels into DI water, but the blisters decreased in size, or were not observable, after the panels were left out in air for a day. Panels with fewer blisters performed better in salt spray testing than panels with many blisters, and the adhesion strength of the MUV was higher on panels with fewer blisters as well.

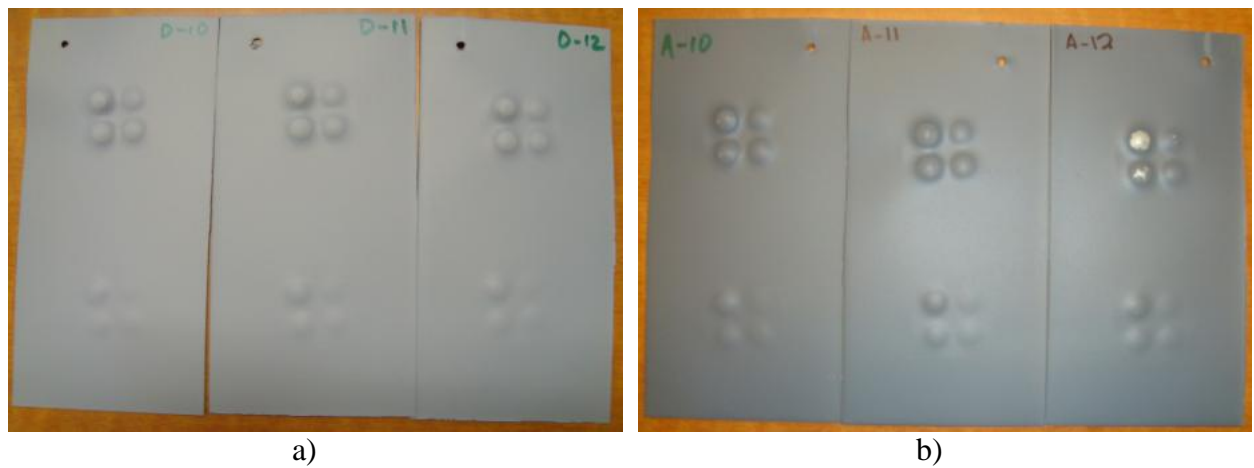


Chromate controls



MUV on CrCC

Figure 55. Optical images of Al 2024-T0 panels after low temperature flexibility tests.



a)

b)

Figure 56. Optical images of Al 2024-T0 panels after room temperature flexibility tests: a) chromate controls and b) MUV on CrCC.

Summary of MUV Evaluations

Table VIII presents an overall summary of the MUV results from the project. The tests that were consistently passed by the MUV coatings during the project are highlighted in blue (Note: the Al 7075 substrates were not used for many of the tests because the specification calls for Al 2024.) Adjustments to MUV formulation throughout the project resulted in the ability of the MUV to pass many of the other tests, including wet tape adhesion and low temperature flexibility. Room temperature flexibility and accelerated weathering values were close to required specifications and did pass requirements in certain instances. The main objective of developing and demonstrating a UV curable coating that can provide corrosion protection to high strength aluminum alloy substrates was achieved.

Table VIII - Summary of MUV Evaluation Results

	Al 2024				Al 7075			
	MUV on CrCC	MUV on CeCC	Non-chrome control	Chrome Control	MUV on CrCC	MUV on CeCC	Non-chrome control	Chrome Control
2000 hours Salt Spray	Pass	Fail	Pass	Pass	Pass	Fail	Pass	Pass
1000 hours Filiform Corrosion	Pass	Fail	Pass	Pass	Pass	Pass	Fail	Pass
Wet Tape Adhesion	Pass	Fail	Fail	Pass	N/A	N/A	N/A	N/A
Room Temperature Flexibility	Fail	Fail	Fail	Pass	N/A	N/A	N/A	N/A
Low Temperature Flexibility	Pass	Fail	Fail	Pass	N/A	N/A	N/A	N/A
Xenon Arc Weathering	Fail	Fail	Pass	Pass	N/A	N/A	N/A	N/A

6. Conclusions and Implications for Future Research/Implementation

The project was successful in achieving many of the goals and objectives in the original proposal. Cerium conversion coatings were able to pass 336 hours of ASTM B117 salt spray testing on Al 2024-T3 and Al 7075-T6 with proper surface preparation, deposition conditions, and post-treatment. It was determined that substrate preparation significantly altered the surface chemical and electrochemical properties of high strength aluminum alloys. Activation of panels in strong acid or base solutions removed the native oxides and exposed intermetallic compounds in the alloys. Acid activation results in faster CeCC deposition rates, reducing the number of spray cycles required to completely cover a substrate from 40 for panels that were degreased to 1 for panels that were degreased and activated. Alternative surface preparation methods such as ultrasonic cleaning, use of abrasive media, and hand application of cleaning solutions, were shown to be suitable for and compatible with subsequent CeCC deposition processes. The addition of 0.8 g gelatin to deposition solutions was found to decrease the effective deposition rate of CeCCs by slowing the nucleation process, improving coating quality and corrosion resistance. Investigations on the effect of the pH, Ce concentration, and amount of H_2O_2 in the deposition solution found that a pH of 2.5, concentration of 4 wt.% Ce using CeCl_3 salt sources, and 20 ml of H_2O_2 resulted in coatings that performed well in salt spray and electrochemical testing and optimized phosphate post-treatment. However, the use of chloride and peroxide containing deposition solutions was found to produce sub-surface crevices in the Al substrates. Phosphate solution post-treatment of CeCCs could significantly improve the corrosion protection of the films. Several phosphate sources and processing conditions were evaluated and it was determined that using $\text{NH}_4\text{H}_2\text{PO}_4$ at pH 4.5 and 85°C for 5 minutes was able to consistently pass ASTM B117 criteria. Correlation of salt spray results and electrochemical polarization and impedance spectroscopy was excellent after modification of a prohesion-based electrolyte. The majority of CeCC depositions were done using a spray method but brush application, immersion, and electrolytic processes were also demonstrated to be effective. In almost all cases, it was found that a $\sim 400\text{nm}$ thick CeCC was the most effective corrosion coating. All of the knowledge gained during the project was used to develop and publish a deposition mechanism for CeCCs that has gained recognition and acceptance within the scientific community.

Development and demonstration that UV curable coatings with inorganic corrosion inhibitors could be fully cured in just a few seconds, have good flexibility, adhesion, and fluid resistance, and pass corrosion testing was a major breakthrough. There was skepticism at the start of the project that highly loaded polymer coatings would be able to pass the requirements for existing epoxy based coatings; therefore, chromate and non-chromate epoxy coatings were used as reference standards throughout the project in order to directly compare results. Evaluation of MUV coatings on TCP conversion coated panels was also done during the project. The multifunctional UV curable system repeatedly passed 3000 hours of ASTM B117 salt spray testing on chromate conversion coated high strength Al alloys with ~ 30 wt. % Hybricor 204 corrosion inhibitor from Wayne Pigments in the MUV. An acrylate-based polymer system was used throughout the project along with a two bulb curing system from Fusion, Inc. Initially, corrosion inhibitors from Deft and Wayne Pigments were evaluated but it was evident from the early stages of the project that Hybricor 204 was the best inhibitor. Application of the MUV was done using a drawdown method during the first two rounds of testing in order to conserve material. A complete non-chrome coating system of Hybricor 204 inhibitor on CeCC did pass

ASTM B117 in the first round of testing. A ladder study was done after the first two rounds in order to determine the optimum amount of Hybricor 204 and, while a range of values between 27 and 36 wt% were all effective at inhibiting corrosion, a 29 wt% loading was chosen to develop a MUV spray formation by considering all of the desired properties. The first spray deposited MUV formulation was done during round three and again demonstrated excellent filiform and salt spray corrosion performance, with ~10% elongation, good adhesion, and low gloss values on chromate conversion coated panels. Panels with MUV on CeCC developed blisters during corrosion testing that led to failure. In an attempt to improve the flexibility of the MUV, lower molecular weight oligomers were used during round 4 and, although corrosion performance was still very good, there was degradation in the non-corrosion related performance of the MUV. The final round of testing was done with a formulation that was a modified version of the formulation used in round 3. Darkening of the MUV during accelerated weathering tests and poor performance on CeCC, as was the case in round 3, were observed in round 5. Positive results from round 5 on chromate conversion coated panels included excellent corrosion protection, good adhesion, samples that passed low temperature flexibility testing, and ~10% reverse impact flexibility at room temperature. Collectively, the results indicated that the MUV coatings were capable of passing most of the required aerospace requirements and that adjustments in formulation were able to alter properties as needed.

The results of this project indicate that a two layer coating system consisting of a non-chromate CeCC and UV curable polymer with inorganic corrosion inhibitors is capable of meeting aerospace coating requirements, as demonstrated in the first round of testing. Additional research is needed understand and optimize the CeCC process and MUV formulation such that reproducible results are obtained. The major conclusions that point to the need for future research are summarized below.

- When deposited on high strength aluminum alloys with CrCCs, MUV coatings demonstrated excellent performance. This combination appears to be ready for demonstration on non-critical components on military aircraft, and implementation of the technology onto specific areas of weapons platforms would not require extensive investment.
- The CeCC and MUV consistently pass independent, individual tests but when combined into a system do not meet specifications. In particular, the elimination of blisters on MUV/CeCC panels during salt spray testing would likely result in passing not only ASTM B117 testing but also significantly improve adhesion and flexibility. Some additional research focused on elimination of peroxide species from CeCCs or integrating the MUV with other non-chromate surface treatments is needed to produce a viable chromium-free system.
- Although the MUV coating passes the most critical performance specifications (i.e., corrosion performance, adhesion, etc.), a color change was observed in accelerated weathering testing. Changing the type of pigment used in the MUV could address the changes in color during accelerated weathering.
- Coating processes were developed to be compatible with field application. However, demonstration of the UV curing system would initially need to be done on a small scale for proof of concept followed by large scale operations based on existing processes in commercial use.

The results of this project have shown that the MUV can meet the important performance criteria for coatings used on military aircraft. The path forward to implement the technology is straightforward and appears to be ready for demonstration/validation.

7. Literature Cited

1. "Corrosion Cost and Preventive Strategies in the United States", Report No. FHWA-RD-01-156, CC Technologies and NACE International, September 30, 2001.
2. "OSHA Proposes Revised Rule on Hexavalent Chromium", OSHA News Release, October 1, 2004.
3. "Electrodeposition of Cerium Based Coatings for Corrosion Protection of Aluminum Alloys", J. O. Stoffer, T.J. O'Keefe, S. P. Sitaram, P. Yu, X. Lin, E. Morris, U.S. Patent 5,932,083, Aug. 3, 1999.
4. "Cerium Based Spontaneous Coating Process For Corrosion Protection of Al Alloys", James O. Stoffer, Thomas J. O'Keefe, Matthew O'Keefe, Eric L. Morris, Scott Hayes, Alex Williams, Berny Rivera, Xuan Lin, Patent # 7,048,807, May 23, 2006.
5. B.R.W. Hinton, D.R. Arnott, N.E. Ryan, *Materials Forum* **9** (3), 162-73 (1986).
6. B. Rivera, B. Johnson, M. O'Keefe, and W. Fahrenholtz, *Surface and Coatings Technology*, **176**(3), 349 (2003).
7. S. Geng, W. Pinc, P. Yu, P. Jones, M. O'Keefe, W. Fahrenholtz, and T. O'Keefe, *J. of Surface Finishing*, 2(4) 276-282 (2007).
8. Pu Yu, Scott A. Hayes, Thomas J. O'Keefe, Matthew J. O'Keefe, and James O. Stoffer, *J. of the Electrochem. Soc.*, **153**(1), C74-79 (2006).
9. "Radiation Curing in Coatings", J. V. Koleske, ASTM International, US, pp.3 (2002).
10. V.Shukla, M.Bajpai, D.K. Singh, M.Singh, R.Shukla, *Pigment & Resin Technology* **33**(5),272 (2004).
11. "New Perspectives in product development and pollution control through the use of ultra violet polymerization", A. De Raeve, <http://www.unitex.be/Downloads/niet-leden/to2c-deraeve.pdf>.
12. "UV curing technical principle and mechanism", Ciba Specialty Chemicals, http://www.cibasc.com/pf/docMDMS.asp?targetlibrary=CHBS_CE_MADS&docnumber=1628.

8. Appendices

8.1 List of Scientific/Technical Publications

A. Articles in Peer Reviewed Journals

1. S. Geng, P. Yu, M O'Keefe, W. Fahrenholtz, and T. O'Keefe, "Screening Study of Spray Solution Parameters for Depositing Cerium Based Conversion Coatings on Al Alloy 2024-T3", J. Applied Electrochemistry, 40, 551, (2010).
2. D. Heller, W. Fahrenholtz, and M. O'Keefe, "The Effect of Post-treatment Time and Temperature on Cerium Based Conversion Coatings on Al 2024-T3", Corrosion Science, 52, 360 (2010).
3. W.R. Pinc, P. Yu, M. O'Keefe, and W. Fahrenholtz, "Effect of Gelatin Additions on the Corrosion Resistance of Cerium Based Conversion Coatings Spray Deposited on Al 2024-T3," Surface and Coatings Technology, 203(23) 3533 (2009).
4. D. Heller, W. Fahrenholtz, and M. O'Keefe, "Effect of Phosphate Source on the Post-treatment and Corrosion Performance of Cerium Based Conversion Coatings on Al 2024-T3", J. Elec. Soc. 156(11), C400 (2009).
5. D.K. Heller, W.G. Fahrenholtz and M.J. O'Keefe, "The Effect of Phosphate Source on the Post-Treatment of Cerium-Based Conversion Coatings on Al 2024-T3 and Its Correlation to Corrosion Performance," ECS Trans. 16, 47 (2009).
6. W. Pinc, S. Geng, M. O'Keefe, W. Fahrenholtz, and T. O'Keefe, "Effects of acid and alkaline based surface preparations on spray deposited cerium based conversion coatings on Al 2024-T3", Applied Surface Science, 255, 4061 (2009).
7. S. Geng, W. Pinc, P. Yu, P. Jones, M. O'Keefe, W. Fahrenholtz, and T. O'Keefe, "Influence of Cleaning on the Deposition Rate of Cerium Based Conversion Coatings on Aluminum Alloy 2024", J. of Surface Finishing, 2(4) 276-282 (2007).
8. P. S. Jones, P. Yu, W.R. Pinc. M.J. O'Keefe, W.G. Fahrenholtz, and T.J. O'Keefe, "Spray Deposition of Cerium Oxide-Based Conversion Coatings on Al 2024-T3," International Journal of Applied Ceramic Technology, 5(1) 63-73 (2008).
9. Shaoxin You, Philip Jones, Ajay Padwal, Paul Yu, Matthew O'Keefe, William Fahrenholtz, and Thomas O'Keefe, "Response of Nano-crystalline Cerium Based Conversion Coatings on Al 2024-T3 To Chloride Environments", Materials Letters, 61 (17), 3378 (2007).

B. Technical Reports

1. Philip Jones, May 2007, MS Thesis, Impact of Processing Parameters on Spray Deposition of a Cerium-Based Conversion Coating on Al 2024-T3
2. William Gammill, December 2009, MS Thesis, Evaluation of Alternative Methods for Surface Preparation and Deposition of Cerium-based Conversion Coatings on Aluminum Alloys
3. "Multifunctional UV (MUV) Curable Corrosion Coatings for Aerospace Applications", Matthew J. O'Keefe, William G. Fahrenholtz, and Ben S. Curatolo, Metal Finishing, pp. 28-31, February 2010.

4. “Cerium-Based Conversion Coatings as Alternatives to Hex Chrome”, Matthew J. O’Keefe, Shujiang Geng, and Simon Joshi, Metal Finishing, pp. 25-28, May 2007.

C. Conference or Symposium Scientifically Recognized

1. A. Thomas, D. Heller, W. Gammill* W. Fahrenholtz, M. O’Keefe, J. DeAntoni, and B. Curatolo, “Performance of Multifunctional UV (MUV) Curable Corrosion Coating Systems to Aerospace Military Test Criteria”, DoD Corrosion Conference, Washington DC, Aug 2009.
2. S. Geng, W. Pinc, S. Joshi, W. Fahrenholtz, M. O’Keefe, T. O’Keefe and P. Yu, “Influence of Processing Parameters on Cerium Based Conversion Coatings”, Tri-Services Corrosion Conference, Denver, CO, Dec 2007.
3. J. DeAntoni, B. Curatolo, M. O’Keefe and W. Fahrenholtz, “Development and Evaluation of Multifunctional Ultraviolet (MUV) Light Curable Coatings for High Strength Aluminum Alloys”, Tri-Services Corrosion Conference, Denver, CO, Dec 2007.
4. Philip Jones, Ajay Padwal, Paul Yu, Matthew J. O’Keefe, William Fahrenholtz, Thomas O’Keefe, “Characterization of Alkaline Cleaned and Cerium Oxide Coated Al 2024-T3”, Materials Science and Technology Conference, Product Manufacturing Symposium, pp 591-597, Cincinnati, OH, Oct 2006.

D. Conference of Symposium Abstracts

1. W. Pinc, D. Heller, W. Fahrenholtz, and M. O’Keefe, “The Electrochemical and Structural Changes of Cerium Based Conversion Coatings During Exposure to a Salt Spray Environment”, Electrochemical Society Meeting, Oct 5-8, 2009, Vienna, Austria.
2. D.K. Heller, W.G. Fahrenholtz, and M.J. O’Keefe, "Electrochemical Analysis of Phosphate Treated Cerium Based Conversion Coatings on Al 2024-T3," PRIME 2008: Pacific Rim Meeting on Electrochemical and Solid State Science, October 12-17, 2008, Honolulu, HI.
3. Heller, W. Fahrenholtz, and M. O’Keefe, “The Effect of Phosphate Post-treatment Process Variables on Cerium Based Conversion Coating of Al 2024-T3”, MS&T Conference, Pittsburgh, PA, Oct 2008.
4. W. Gammill, W. Fahrenholtz, and M. O’Keefe, “Non-Immersion Surface Preparation for Cerium-based Conversion Coatings On Aluminum Substrates”, MS&T Conference, Pittsburgh, PA, Oct 2008.
5. S. Joshi, W. Fahrenholtz, and M. O’Keefe, “The Effect of Phosphate Additions on the Corrosion Resistance of Cerium Conversion Coatings on Aluminum Alloy 7075 – T6”, MS&T Conference, Pittsburgh, PA, Oct 2008.
6. W. Pinc, W. Fahrenholtz, and M. O’Keefe, “Effect of Gelatin Additions on the Corrosion Resistance of Cerium Based Conversion Coatings”, MS&T Conference, Pittsburgh, PA, Oct 2008.
7. S. Geng, P. Yu, M. O’Keefe, W. Fahrenholtz, and T. O’Keefe, “Corrosion Behavior of Ce-Based Conversion Coatings on Al Alloy 2024-T3”, MS&T Conference, Detroit, MI, Sep 2007.

8. S. Joshi, W. Pinc, S. Geng, M. O'Keefe, W. Fahrenholtz, and T. O'Keefe, "Characterization of Cerium Conversion Coated Al 7075-T6 Prepared with Alkaline and Acid Cleaning Solutions", MS&T Conference, Detroit, MI, Sep 2007.
9. Materials Science and Technology (MS&T) Conference, "Corrosion Performance of Cerium-Based Conversion Coatings on Aluminum Alloys", Bill Fahrenholtz and Matt O'Keefe, Oct 28, 2009.
10. SERDP 2008 Symposium, "Development and Evaluation of Multifunctional UV (MUV) Curable, Non-Chromate Corrosion Coating Systems", Matt O'Keefe, Bill Fahrenholtz, John DeAntoni, and Ben Curatolo, Wash DC, Dec 3, 2008.
11. University of Cincinnati, Materials Science and Engineering Seminar, "Non-Chromate Coatings for Corrosion Protection", Matt O'Keefe and Bill Fahrenholtz, 8 May 2008.
12. Surface Finishing and Repair Issues for Sustaining New Military Aircraft Workshop, "Multifunctional UV Coatings and Ce-Based Materials", Matt O'Keefe, Bill Fahrenholtz, John DeAntoni, and Ben Curatolo, Tempe, AZ, Feb 28 2008.
13. DoD Metal Finishing Workshop, "Ce Based Conversion Coatings", Matt O'Keefe, Hill AFB, UT, May 16, 2007.
14. GM Tech Center Symposium, "Development of Environmentally Friendly Corrosion Coating Systems", Matt O'Keefe, Warren, MI, Apr 16, 2007.
15. W. Pinc, S. Geng, S. Joshi, M. O'Keefe, W. Fahrenholtz, and T. O'Keefe, "Effects of Acidic and Alkaline Based Surface Preparations of Al 2024-T3 on Spray Deposited Cerium-Oxide Conversion Coatings", MS&T Conference, Detroit, MI, Sep 2007.